

Rigorous Homogenization of a Stokes-Nernst-Planck-Poisson Problem for various Boundary Conditions

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Abstract

We perform the periodic homogenization (i. e. $\varepsilon \rightarrow 0$) of the non-stationary Stokes-Nernst-Planck-Poisson system using two-scale convergence, where ε is a suitable scale parameter. The objective is to investigate the influence of *different boundary conditions and variable choices of scalings in ε* of the microscopic system of partial differential equations on the structure of the (upscaled) limit model equations. Due to the specific nonlinear coupling of the underlying equations, special attention has to be paid when passing to the limit in the electrostatic drift term. As a direct result of the homogenization procedure, various classes of upscaled model equations are obtained.

Keywords: Homogenization, Stokes-Nernst-Planck-Poisson system, colloidal transport, porous media, two-scale convergence

AMS subject classification: 35B27, 76M50, 76Sxx, 76Rxx, 76Wxx

1. Introduction

This paper deals with the periodic homogenization of a non-stationary Stokes-Nernst-Planck-Poisson-type system (SNPP). The real-world applications that fit to this context include areas of colloid chemistry, electro-hydrodynamics and semiconductor devices. Our interest lies in the theoretical understanding of colloid enhanced contaminant transport in the soil. Colloidal particles are under consideration for quite a long time since they are very important in multiple applications ranging from waste water treatment, food industry, to printing, etc. The monograph of van de Ven [30] and the books by Elimelech [11] and Hunter [15] yield a well founded description of colloidal particles and their properties. However, the different processes determining the dynamics of colloids within a heterogenous porous medium are not yet completely understood. Therefore, the mathematically founded forecast of contaminant transport within soils is still very difficult, as it is strongly influenced by the movement and distribution of colloidal particles (cf. e. g. [29]).

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Using mathematical homogenization theory, different kinds of coupled models have been investigated/derived. Besides the combination of fluid flow and convective-diffusive transport, the coupling among different kinds of species by chemical reactions have been discussed for example in [12], see also the references cited therein. Further cross couplings of the water flow by heat, chemical or electrostatical transport are studied formally in [4]. It is worth pointing out a totally different context, where a nonlinear coupling quite analogous to the one of our problem occurs – the phase-field models of Allen-Cahn type, see [10] for more details on the modeling, analysis, and averaging of such models. Investigations concerning variable scaling and their influence on the limit equations is illustrated (by means of formal two-scale asymptotic homogenization) in [3], where different choices of ranges of the Péclet number are considered. In the same spirit, but this time rigorously, different scale ranges are examined for a linear diffusion-reaction system with interfacial exchange in [24]. Moreover, hybrid mixture theory has been applied to swelling porous media with charged particles in [5] and [6]. Formal upscaling attempts of the Nernst-Planck-Poisson system using formal asymptotic expansion are reported, for instance, in [4], [17], [20] and [21]. It is worth pointing out that [20] and [21] succeed to compute (again formally) microstructure effects on the deforming, swelling clay. In spite of such a good formal asymptotic understanding of the situation, rigorous homogenization results seem to be lacking. Only recently, Schmuck published a paper concerning the rigorous upscaling of a non-scaled Stokes-Nernst-Planck-Poisson system with transmission conditions for the electrostatic potential, [28]. Furthermore, Allaire et al. studied the stationary and linearized case in [2]. Our paper contributes in this direction since we perform the rigorous homogenization of the SNPP system for different boundary conditions as well as for variable choices of scalings in ε , where ε is a scale parameter referring to a (periodically-distributed) microstructure. The main focus of the paper thereby lies on the investigation of the influence of the boundary condition and scalings in ε on the structure of the effective limit equations. This paper is built on [25]. However, we corrected essential errors concerning the use of Poincaré’s inequality. Furthermore, we introduce suitable redefinitions of the electrostatic potential in order to provide a more clearly arranged form of our homogenization results. Most important for the applications, we extend our results for different choices of boundary conditions for the electrostatic potential and include Stokes equations to our analysis in order to describe the interactions with the fluid flow.

The paper is organized in the following way: In Section 2, we present the underlying microscopic model equations – the Stokes-Nernst-Planck-Poisson system. This is the starting point of our investigations. The Nernst-Planck equations describe the transport (diffusion, convection and electrostatic drift) of and reaction between (number) densities of colloidal particles. The electrostatic potential is given as a solution of Poisson’s equation with the charge density which is created by the colloidal particles as forcing term. The fluid flow is determined by a modified Stokes equa-

tion. Basic results concerning existence and uniqueness of weak solutions of this coupled system of partial differential equations are stated in Theorem 3.7 in Section 3. Moreover, Section 3 contains the definition of the basic heterogeneous and periodic geometric setting. The (small) scale parameter ε introduced here balances different physical terms in the system of partial differential equations and plays a crucial role in the homogenization procedure. Furthermore, ε independent *a priori* estimates are shown for both Neumann and Dirichlet boundary conditions of the electrostatic potential in Theorem 3.5 and Theorem 3.6. In Section 4, we state the basic definitions and well known compactness results concerning the method of two-scale convergence. The main idea is to obtain an “equivalent” system of partial differential equations that can reasonably describe the effective macroscopic behavior of the considered phenomena. We achieve this by investigating rigorously the limit $\varepsilon \rightarrow 0$ using two-scale convergence. Our analysis focuses on the influence of the choice of the boundary condition for the electrostatic potential and the different choices of scalings in ε on both the *a priori* estimates and the structure of the limit problems. The main calculations are included in Section 4.1 and Section 4.2. The crucial point is the nonlinear coupling of the system of partial differential equations by means of the electrostatic potential, and therefore, the passage to the limit $\varepsilon \rightarrow 0$ in the nonlinear transport terms of the Nernst-Planck equations and the Stokes equation. The main result (Theorems 4.5, 4.7, 4.9 and Theorems 4.11, 4.13, 4.15) of the paper discuss for which choices of scaling we can pass rigorously to the limit $\varepsilon \rightarrow 0$. The results of this homogenization procedure and the structure of the limit equations are emphasized in Remarks 4, 5, 7 and 8, 9, 11 and in Section 5.

2. The Underlying Physical Model

We list in Table 1 all variables and physical parameters that are used in the following including their dimensions. Thereby, L is a unit of length, T a unit of time, M stands for a unit of mass, C for a unit of charge, while K represents the unit of temperature.

In this section, we formulate a system of partial differential equations describing colloid dynamics. Following e.g. [11] and [30], we impose to our system the balance of mass as well as the conservation of electrostatical charges. Note that in most applications, colloidal particles are charged [30]. Besides standard transport mechanisms (convection and diffusion), a charged dispersion of colloidal particles is also transported by the electrostatic field created by the particles themselves as well as by the possibly charged soil matrix. Further interaction potentials (e.g. van-der-Waals forces or an externally applied electrostatic field) may also act on the colloidal particles. Throughout this paper we neglect the latter effects and focus on the investigations of the intrinsic electrostatic interaction. Following Chapter 3.3 in [30], the positively (+) and negatively (-) charged particles are modeled in an Eulerian approach by some number density c^\pm , which is transported by the total velocity v^\pm that consists of two parts: First, the convective velocity term v^{hydr}

v	$[L/T]$	velocity
p	$[M/L/T^2]$	pressure
η	$[M/L/T]$	kinematic viscosity of the fluid
ρ	$[M/L^3]$	density of the fluid
c	$[1/L^3]$	number density
D	$[L^2/T]$	diffusivity
ν	$[-]$	outer unit normal
Φ	$[V] := [ML^2/T^2/C]$	electrostatic potential
σ	$[ML/T^2/C]$	surface charge density
z	$[-]$	charge number
e	$[C]$	elementary charge
$\epsilon_0 \epsilon_r$	$[C/V/L]$	dielectrostatic permittivity · relative permittivity
k	$[ML^2/T^2/K]$	Boltzmann constant
T	$[K]$	absolute temperature

Table 1: List of the variables and physical parameters and their dimensions.

due to the fluid flow within the porous medium in which the colloidal particles are transported. This is the same for all types of charge carriers. Second, the drift term $v^{\text{drift},\pm}$, that is different for both kinds of charge carriers, can be calculated from the drift force $F^{\text{drift},\pm} = -z^\pm e \nabla \Phi$ via

$$v^{\text{drift},\pm} = f^\pm F^{\text{drift},\pm} = -f^\pm z^\pm e \nabla \Phi$$

with proportionality coefficient f^\pm and an electrostatic interaction potential Φ . In applications, f^\pm is sometimes also called electrophoretic mobility and is related further to the diffusivity D^\pm by the Stokes-Einstein relation $f^\pm = \frac{D^\pm}{kT}$, [30]. The total velocity v^\pm can therefore be expressed by

$$v^\pm = v^{\text{drift},\pm} + v^{\text{hydr}} = -\frac{D^\pm z^\pm e}{kT} \nabla \Phi + v^{\text{hydr}}.$$

Inserting this expression into the standard convection-diffusion-reaction equation for a number density c^\pm results in a modified transport equation which is also known as Nernst-Planck equation. On the boundary Γ of the considered domain Ω we assume no-flux condition, which supplements the so called “no penetration” model, described in [11]. Together with an appropriate choice of the initial conditions $c^{\pm,0}$, the transport of the charged particles can be described properly by the following equations:

$$\partial_t c^\pm + \nabla \cdot \left(v^{\text{hydr}} c^\pm - D^\pm \nabla c^\pm - \frac{D^\pm z^\pm e}{kT} c^\pm \nabla \Phi \right) = R^\pm(c) \quad \text{in } (0, T) \times \Omega, \quad (1a)$$

$$\left(-v^{\text{hydr}} c^\pm + D c^\pm \nabla c^\pm + \frac{D^\pm z^\pm e}{kT} c^\pm \nabla \Phi \right) \cdot \nu = 0 \quad \text{on } (0, T) \times \Gamma, \quad (1b)$$

$$c^\pm = c^{\pm,0} \quad \text{in } \{t = 0\} \times \Omega. \quad (1c)$$

with $c := (c^+, c^-)$. The right-hand side R^\pm in the Nernst-Planck equation include chemical reactions between the particles, source terms et cetera.

The electrostatic interaction potential Φ has to be calculated using Poisson’s equation (2a). The effect on the electrostatic field implied by the charged particles themselves is included as right-hand

side. This equation may be supplemented by Neumann or Dirichlet boundary conditions which correspond to the surface charge and the so called ζ potential of the solid matrix, respectively. Depending on the application in the geosciences either of the boundary conditions is given for example by measurements.

$$-\Delta\Phi = \frac{e}{\epsilon_0\epsilon_r} (z^+c^+ - z^-c^-) \quad \text{in } (0, T) \times \Omega, \quad (2a)$$

$$\nabla\Phi \cdot \nu = \sigma \quad \text{on } (0, T) \times \Gamma_N, \quad (2b)$$

$$\Phi = \Phi_D \quad \text{on } (0, T) \times \Gamma_D. \quad (2c)$$

In order to determine the fluid velocity v^{hydr} we solve the modified Stokes' equations for incompressible fluid flow (3a), 3b. As force term on the right hand side we take into account the drift force density. These equations are supplemented by a no slip boundary condition.

$$-\eta\Delta v^{\text{hydr}} + \frac{1}{\rho}\nabla p = -\frac{e}{\rho}(z^+c^+ - z^-c^-)\nabla\varphi^{\text{el}} \quad \text{in } (0, T) \times \Omega \quad (3a)$$

$$\nabla \cdot v^{\text{hydr}} = 0 \quad \text{in } (0, T) \times \Omega \quad (3b)$$

$$v^{\text{hydr}} = 0 \quad \text{on } (0, T) \times \Gamma. \quad (3c)$$

Remark 1. (Part of) the system (1), (2), (3) arises in more general contexts. It plays a role when determining ion distributions (for example around colloidal particles or in a ion channel) and also in the framework of semiconductor devices especially if the convective term is neglected. We refer the reader to [19], [26] for aspects on the modeling and analysis of the semiconductor equations.

3. Pore Scale Model P_ϵ

In this section, we incorporate the physical processes described in Section 2 in a multi-scale framework and state basic properties of weak solutions as well as results concerning solvability of our problem. On the one hand, the phenomena considered in Section 2 take place on the microscale and, on the other hand, the physical behavior we are interested in occurs on a macroscopic domain. In the framework of colloids, the transport takes place within the pore space of a porous medium that is defined by its soil matrix. The definition of the idealized underlying geometry which characterizes the highly heterogenous porous structure is depicted in Figure 1. The (small) scale parameter ϵ is introduced to scale/balance the different terms in the governing system of partial differential equations (1), (2) and (3).

Let us consider a bounded and connected domain $\Omega \subset \mathbb{R}^n$, $n \in \mathbb{N}$ with an associated periodic microstructure defined by the unit cell $Y = (0, 1)^n$. In the following we only consider the physically meaningful space dimensions $n \in \{1, 2, 3\}$. The unit cell Y is made up of two open sets, see Figure 1: The liquid part Y_l and the solid part Y_s such that $\bar{Y}_l \cup \bar{Y}_s = \bar{Y}$ and $Y_l \cap Y_s = \emptyset$, $\bar{Y}_l \cap \bar{Y}_s = \Gamma$. Especially, the solid part does not touch the boundary of the unit cell Y and therefore the fluid part is connected. We call $\epsilon < 1$ the scale parameter and assume the macroscopic domain to be

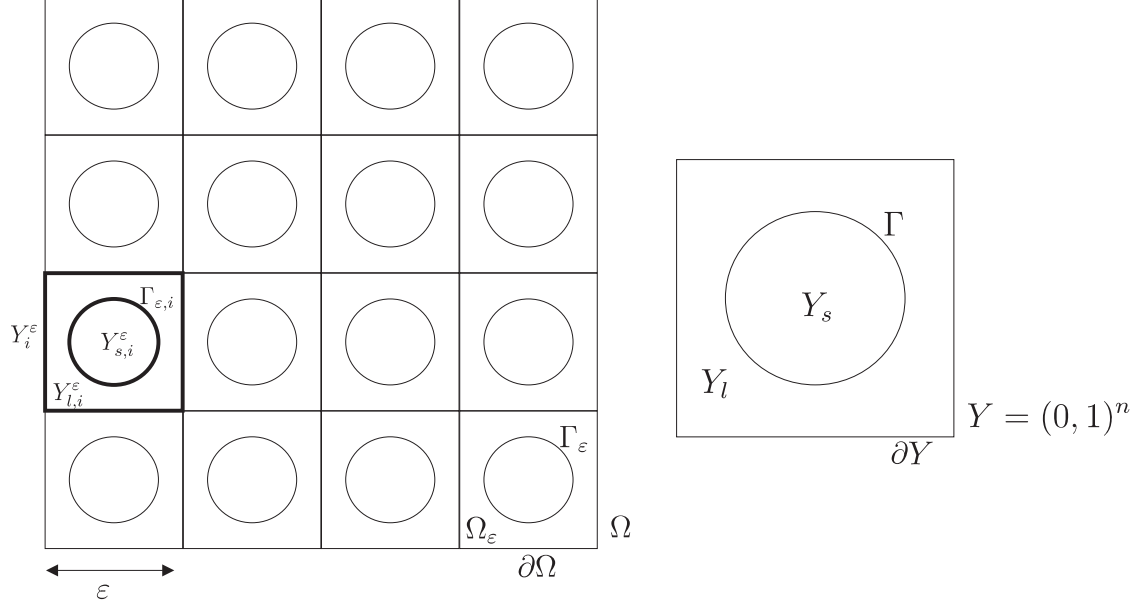


Figure 1: Standard unit cell (left) and periodic representation of a porous medium (right).

covered by a regular mesh of size ε consisting of ε scaled and shifted cells Y_i^ε that are divided into an analogously scaled fluid part, solid part and boundary. Let us denote these by $Y_{l,i}^\varepsilon$, $Y_{s,i}^\varepsilon$, and $\Gamma_{\varepsilon,i}$, respectively. The fluid part/pore space, the solid part and the inner boundary of the porous medium are defined by

$$\Omega_\varepsilon := \bigcup_i Y_{l,i}^\varepsilon, \quad \Omega \setminus \overline{\Omega}_\varepsilon := \bigcup_i Y_{s,i}^\varepsilon, \quad \text{and} \quad \Gamma_\varepsilon := \bigcup_i \Gamma_{\varepsilon,i}.$$

Consequently, since we assume that Ω is completely covered by ε -scaled unit cells Y_i^ε and, in particular, since the solid part is not allowed to intersect the outer boundary, i.e. $\partial\Omega \cap \Gamma_\varepsilon = \emptyset$.

The objective of the paper is to rigorously investigate the limit $\varepsilon \rightarrow 0$. The focus thereby lies on the coupling between the colloidal transport, the fluid flow and the electrostatic potential. We weight the different terms in (1), (2) and (3) with the scale parameter ε in order to derive reasonable macroscopic model equations. In the framework of colloids, a non-dimensionalization procedure which can be used to motivate the choice of scaling has been done for example in [30]. However, since the system (1), (2) and (3) is used to describe various kinds of applications, different choices of scaling may be interesting depending on the underlying physical problem. We focus on the influence of the nonlinear coupling of the SNPP system due to the electrostatic potential and therefore regard Neumann as well as Dirichlet boundary condition for the Poisson equation and consider only the scaling of the coupling terms. For the ease of presentation, we assume that $D := D^+ = D^-$ and $z := z^+ = -z^-$ and suppress here the (constant) parameters $\eta, \rho, z, e, k, T, D, \epsilon_r, \epsilon_0$ as well as the superscript hydr within all the equations. The resulting system of scaled partial differential

equations is referred here as Problem P_ε :

$$-\varepsilon^2 \Delta v_\varepsilon + \nabla p_\varepsilon = -\varepsilon^\beta (c_\varepsilon^+ - c_\varepsilon^-) \nabla \Phi_\varepsilon \quad \text{in } (0, T) \times \Omega_\varepsilon, \quad (4a)$$

$$\nabla \cdot v_\varepsilon = 0 \quad \text{in } (0, T) \times \Omega_\varepsilon, \quad (4b)$$

$$v_\varepsilon = 0 \quad \text{on } (0, T) \times (\Gamma_\varepsilon \cup \partial\Omega), \quad (4c)$$

$$-\varepsilon^\alpha \Delta \Phi_\varepsilon = c_\varepsilon^+ - c_\varepsilon^- \quad \text{in } (0, T) \times \Omega_\varepsilon, \quad (4d)$$

$$\varepsilon^\alpha \nabla \Phi_\varepsilon \cdot \nu = \varepsilon \sigma \quad \text{on } (0, T) \times \Gamma_{\varepsilon, N}, \quad (4e)$$

$$\Phi_\varepsilon = \Phi_D \quad \text{on } (0, T) \times \Gamma_{\varepsilon, D}, \quad (4f)$$

$$\varepsilon^\alpha \nabla \Phi_\varepsilon \cdot \nu = 0 \quad \text{on } (0, T) \times \partial\Omega, \quad (4g)$$

$$\partial_t c_\varepsilon^\pm + \nabla \cdot (v_\varepsilon c_\varepsilon^\pm - \nabla c_\varepsilon^\pm \mp \varepsilon^\gamma c_\varepsilon^\pm \nabla \Phi_\varepsilon) = R_\varepsilon^\pm(c_\varepsilon^+, c_\varepsilon^-) \quad \text{in } (0, T) \times \Omega_\varepsilon, \quad (4h)$$

$$(-v_\varepsilon c_\varepsilon^\pm + \nabla c_\varepsilon^\pm \pm \varepsilon^\gamma c_\varepsilon^\pm \nabla \Phi_\varepsilon) \cdot \nu = 0 \quad \text{on } (0, T) \times (\Gamma_\varepsilon \cup \partial\Omega), \quad (4i)$$

$$c_\varepsilon^\pm = c^{\pm, 0} \quad \text{in } \{t = 0\} \times \Omega_\varepsilon. \quad (4j)$$

with the volume additivity constraint $c_\varepsilon^+ - c_\varepsilon^- = 1$ which is quite standard for the system (4), see e.g. [26]. This constraint can be relaxed in the case of Neumann boundary condition for the electrostatic potential, for the homogenous case see also [27].

Remark 2. We could add a variable scaling also for the convective, diffusive and reactive terms. However, we concentrate on the role of the electrostatic potential Φ_ε . The same choice of scaling in the equations for c_ε^\pm is especially justified in the case that both types of particles have similar properties except of the sign of the charge. On the outer boundary $\partial\Omega$ we assume homogenous flux conditions for the concentration fields and the electrostatic potential as well as no slip boundary conditions for the velocity field. However, different linear boundary conditions could be chosen instead without notable changes in the calculations. For a discussion on different boundary conditions on the inner boundary and their influence on the results of the homogenization procedure we refer to the discussions in Remark 4, 5, 7 and 8, 9, 11 and in Section 5.

Multiplying the system of equations (4) with the test functions $\varphi_1 \in (H_0^1(\Omega_\varepsilon))^n, \varphi_2, \varphi_3, \psi \in H^1(\Omega_\varepsilon)$ and integrating by parts we get the following weak formulation of Problem P_ε :

$$\int_{\Omega_\varepsilon} \varepsilon^2 \nabla v_\varepsilon \cdot \nabla \varphi_1 - p_\varepsilon \nabla \cdot \varphi_1 dx = \int_{\Omega_\varepsilon} -\varepsilon^\beta (c_\varepsilon^+ - c_\varepsilon^-) \nabla \Phi_\varepsilon \cdot \varphi_1 dx \quad (5a)$$

$$\int_{\Omega_\varepsilon} v_\varepsilon \cdot \nabla \psi dx = 0 \quad (5b)$$

$$\int_{\Omega_\varepsilon} \varepsilon^\alpha \nabla \Phi_\varepsilon \cdot \nabla \varphi_2 dx - \int_{\Gamma_\varepsilon} \varepsilon^\alpha \nabla \Phi_\varepsilon \cdot \nu \varphi_2 dx = \int_{\Omega_\varepsilon} (c_\varepsilon^+ - c_\varepsilon^-) \varphi_2 dx, \quad (5c)$$

$$\langle \partial_t c_\varepsilon^\pm, \varphi_3 \rangle_{(H^1)', H^1} + \int_{\Omega_\varepsilon} (-v_\varepsilon c_\varepsilon^\pm + \nabla c_\varepsilon^\pm \pm \varepsilon^\gamma c_\varepsilon^\pm \nabla \Phi_\varepsilon) \cdot \nabla \varphi_3 dx = \int_{\Omega_\varepsilon} R_\varepsilon^\pm(c_\varepsilon^+, c_\varepsilon^-) \varphi_3 dx. \quad (5d)$$

Definition 3.1. We call $(v_\varepsilon, p_\varepsilon, \Phi_\varepsilon, c_\varepsilon^+, c_\varepsilon^-)$ a weak solution of Problem P_ε if $v_\varepsilon \in L^\infty(0, T; H_0^1(\Omega_\varepsilon))$, $p_\varepsilon \in L^\infty(0, T; L^2(\Omega_\varepsilon))$, $\Phi_\varepsilon \in L^\infty(0, T; H^1(\Omega_\varepsilon))$ and $c_\varepsilon^\pm \in L^\infty(0, T; L^2(\Omega_\varepsilon)) \cap L^2(0, T; H^1(\Omega_\varepsilon))$

with $\partial_t c_\varepsilon^\pm \in L^2(0, T; (H^1(\Omega_\varepsilon))')$ and equations (5) are satisfied for all test functions $\varphi_1 \in (H_0^1(\Omega_\varepsilon))^n$, $\varphi_2, \varphi_3, \psi \in H^1(\Omega_\varepsilon)$.

We modify the drift term in the Nernst-Planck equation by replacing the concentration fields c_ε^\pm with the cut off functions $\tilde{c}_\varepsilon^\pm := \max(0, c_\varepsilon^\pm)$:

$$\partial_t c_\varepsilon^\pm + \nabla \cdot (v_\varepsilon c_\varepsilon^\pm - \nabla c_\varepsilon^\pm \mp \varepsilon^\gamma \tilde{c}_\varepsilon^\pm \nabla \Phi_\varepsilon) = R_\varepsilon^\pm(c_\varepsilon^+, c_\varepsilon^-) \quad \text{in } (0, T) \times \Omega_\varepsilon, \quad (6a)$$

$$(-v_\varepsilon c_\varepsilon^\pm + \nabla c_\varepsilon^\pm \pm \varepsilon^\gamma \tilde{c}_\varepsilon^\pm \nabla \Phi_\varepsilon) \cdot \nu = 0 \quad \text{in } (0, T) \times (\Gamma_\varepsilon \cup \partial\Omega), \quad (6b)$$

$$c_\varepsilon^\pm = c^{\pm, 0} \quad \text{in } \{t = 0\} \times \Omega_\varepsilon. \quad (6c)$$

The modified system consisting of (6) and (4a)-(4g) is referred here as Problem \tilde{P}_ε . The weak solution of Problem \tilde{P}_ε is defined analogously to Definition 3.1.

Remark 3. The weak solution of Problem \tilde{P}_ε is also a weak solution of Problem P_ε . Furthermore, all non-negative weak solutions of Problem P_ε are also weak solutions of Problem \tilde{P}_ε . As stated in Theorem 3.7 Problem P_ε has a unique solution which is the non-negative one. Therefore both problems are equivalent.

To be able to state a result on the existence and uniqueness of weak solutions of Problem P_ε , we assume the following additional restrictions for the ease of presentation. Especially item 2 and 4 can be relaxed. Note that, e. g., nonlinear monotonic reaction terms can be handled using homogenization theory as treated in [14].

Assumption 1.

1. *On the geometry:* We assume a perforated domain as introduced in Section 3, i. e. the pore space Ω_ε is bounded, connected and has $C^{0,1}$ -boundary.
2. *On the rate coefficients:* The reaction rates are assumed to have the following structure $R^\pm(c_\varepsilon^+, c_\varepsilon^-) = \mp(c_\varepsilon^+ - c_\varepsilon^-)$. Especially, they are linear and employ conservation of mass for the concentration fields.
3. *On the initial data:* We assume the initial data to be non-negative and bounded independently of ε , i. e.

$$0 \leq c^{\pm, 0}(x) \leq \Lambda \quad \text{for all } x \in \Omega.$$

Furthermore we assume the following compatibility condition for the initial data, i. e.

$$\int_{\Omega_\varepsilon} c^{+, 0} - c^{-, 0} dx = \int_{\Gamma_\varepsilon} \sigma do_x$$

If $\sigma = 0$ this implies global electro neutrality for the initial concentrations.

4. *On the boundary data:* We assume the boundary data σ and Φ_D to be constant.

In order to ensure unique weak solutions, we additionally require

Assumption 2. If the electrostatic potential Φ_ε is determined via the equations (4d), (4e) and (4g), we assume the potential Φ_ε to have zero mean value, i. e. $\int_{\Omega_\varepsilon} \Phi_\varepsilon dx = 0$. Furthermore, we assume the pressure p_ε to have zero mean value, i. e. $\int_{\Omega_\varepsilon} p_\varepsilon dx = 0$.

Theorem 3.2. Let $(v_\varepsilon, p_\varepsilon, \Phi_\varepsilon, c_\varepsilon^+, c_\varepsilon^-)$ be a weak solution of Problem P_ε in the sense of Definition 3.1. Let furthermore Assumption 1 hold. Then the total mass $M = \int_{\Omega_\varepsilon} c_\varepsilon^+ + c_\varepsilon^- dx$ is conserved.

PROOF. We test the Nernst-Planck equations (5d) with $\varphi_3 = 1$, sum over \pm and insert the structure of the reaction rates according to Assumption 1 which directly gives the statement of Theorem 3.2.

Theorem 3.3. Let $(v_\varepsilon, p_\varepsilon, \Phi_\varepsilon, c_\varepsilon^+, c_\varepsilon^-)$ be a weak solution of Problem \tilde{P}_ε . Let furthermore Assumption 1 hold. Then the concentration fields are non-negative, i.e. are bounded from below uniformly in ε .

PROOF. We test the Nernst-Planck equations (5d) with $\varphi_3 = (c_\varepsilon^\pm)_- := \min(0, c_\varepsilon^\pm)$ which yields

$$\int_{\Omega_\varepsilon} \partial_t c_\varepsilon^\pm (c_\varepsilon^\pm)_- - v_\varepsilon c_\varepsilon^\pm \cdot \nabla (c_\varepsilon^\pm)_- + \nabla c_\varepsilon^\pm \cdot \nabla (c_\varepsilon^\pm)_- \pm \varepsilon^\gamma \tilde{c}_\varepsilon^\pm \nabla \Phi_\varepsilon \cdot \nabla (c_\varepsilon^\pm)_- dx = \int_{\Omega} R_\varepsilon^\pm (c_\varepsilon^\pm)_- dx.$$

The drift term cancels directly due to the definition of the cut off function $\tilde{c}_\varepsilon^\pm$. The velocity term cancels by standard calculations due to the incompressibility and no slip boundary condition. After summation over \pm , we have

$$\begin{aligned} \frac{1}{2} \frac{d}{dt} \left(\|(c_\varepsilon^+)_-\|_{L^2(\Omega_\varepsilon)}^2 + \|(c_\varepsilon^-)_-\|_{L^2(\Omega_\varepsilon)}^2 \right) &+ \left(\|\nabla c_\varepsilon^+\|_{L^2(\Omega_\varepsilon)}^2 + \|\nabla c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)}^2 \right) \\ &= \int_{\Omega} -(c_\varepsilon^+ - c_\varepsilon^-)(c_\varepsilon^+)_- + (c_\varepsilon^+ - c_\varepsilon^-)(c_\varepsilon^-)_- dx. \end{aligned}$$

We consider the reaction term $I_R := -(c_\varepsilon^+ - c_\varepsilon^-)(c_\varepsilon^+)_- + (c_\varepsilon^+ - c_\varepsilon^-)(c_\varepsilon^-)_-$ for the following cases:

1. $c_\varepsilon^+ > 0, c_\varepsilon^- > 0$: $I_R = 0$
2. $c_\varepsilon^+ \leq 0, c_\varepsilon^- > 0$: $I_R = -(c_\varepsilon^+ - c_\varepsilon^-)c_\varepsilon^+ \leq 0$
3. $c_\varepsilon^+ > 0, c_\varepsilon^- \leq 0$: $I_R = (c_\varepsilon^+ - c_\varepsilon^-)c_\varepsilon^- \leq 0$
4. $c_\varepsilon^+ \leq 0, c_\varepsilon^- \leq 0$: $I_R = -(c_\varepsilon^+ - c_\varepsilon^-)c_\varepsilon^+ + (c_\varepsilon^+ - c_\varepsilon^-)c_\varepsilon^- = -(c_\varepsilon^+ - c_\varepsilon^-)^2 \leq 0$

In any case we have the estimate $I_R \leq 0$ and therefore

$$\frac{1}{2} \frac{d}{dt} \left(\|(c_\varepsilon^+)_-\|_{L^2(\Omega_\varepsilon)}^2 + \|(c_\varepsilon^-)_-\|_{L^2(\Omega_\varepsilon)}^2 \right) + \left(\|\nabla c_\varepsilon^+\|_{L^2(\Omega_\varepsilon)}^2 + \|\nabla c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)}^2 \right) \leq 0$$

Gronwall's lemma implies the statement of Theorem 3.3 since the initial concentrations are non-negative according to Assumption 1.

Theorem 3.4. Let $(v_\varepsilon, p_\varepsilon, \Phi_\varepsilon, c_\varepsilon^+, c_\varepsilon^-)$ be a weak solution of Problem \tilde{P}_ε . Let furthermore Assumption 1 hold. Then the concentration fields are bounded from above uniformly in ε .

PROOF. The statement of Theorem 3.4 follows directly from Theorem 3.3 combined with the volume additivity constraint $c_\varepsilon^+ + c_\varepsilon^- = 1$. The boundedness of the concentration fields c_ε^\pm can be proven in the case of Neumann boundary conditions for the electrostatic potential without the volume additivity constraint, for the homogenous case see Lemma 3.3.6. in [27] where Moser's iteration technique is applied formally. This formal proof can directly be extended to non-homogenous boundary conditions and linear reaction rates as defined in Assumption 1 and also be made rigorous. A rigorous approach using Moser's iteration can be found for general nonlinear equation in [16]. However, an alternative and more straight forward way is to show that a maximum principle applies in the case of homogenous Neumann boundary conditions for the electrostatic potential. Since the solutions c_ε^\pm of Problem \tilde{P}_ε are non negative, $\tilde{c}_\varepsilon^\pm$ can be replaced by c_ε^\pm in the the Nernst-Planck equations. Using $\varphi_3 = (c_\varepsilon^\pm - \Lambda)_+ := \max(0, c_\varepsilon^\pm - \Lambda)$ as test function, we obtain

$$\begin{aligned} \int_{\Omega_\varepsilon} \partial_t c_\varepsilon^\pm (c_\varepsilon^\pm - \Lambda)_+ - v_\varepsilon c_\varepsilon^\pm \cdot \nabla (c_\varepsilon^\pm - \Lambda)_+ + \nabla c_\varepsilon^\pm \cdot \nabla (c_\varepsilon^\pm - \Lambda)_+ \pm \varepsilon^\gamma c_\varepsilon^\pm \nabla \Phi_\varepsilon \cdot \nabla (c_\varepsilon^\pm - \Lambda)_+ dx \\ = \int_{\Omega_\varepsilon} R_\varepsilon^\pm (c_\varepsilon^\pm - \Lambda)_+ dx \end{aligned}$$

The velocity term cancels by standard calculations due to the incompressibility and no slip boundary condition and it remains

$$\begin{aligned} \frac{1}{2} \frac{d}{dt} \|(c_\varepsilon^\pm - \Lambda)_+\|_{L^2(\Omega_\varepsilon)}^2 + \|\nabla (c_\varepsilon^\pm - \Lambda)_+\|_{L^2(\Omega_\varepsilon)}^2 \\ \pm \varepsilon^\gamma \int_{\Omega_\varepsilon} (c_\varepsilon^\pm - \Lambda) \nabla \Phi_\varepsilon \cdot \nabla (c_\varepsilon^\pm - \Lambda)_+ + \Lambda \nabla \Phi_\varepsilon \cdot \nabla (c_\varepsilon^\pm - \Lambda)_+ dx = \int_{\Omega} R_\varepsilon^\pm (c_\varepsilon^\pm - \Lambda)_+ dx \end{aligned}$$

We consider the drift term separately. Using the identity $(c_\varepsilon^\pm - \Lambda) \nabla \Phi_\varepsilon \cdot \nabla (c_\varepsilon^\pm - \Lambda)_+ = \nabla \Phi_\varepsilon \cdot \frac{1}{2} \nabla (c_\varepsilon^\pm - \Lambda)_+^2$ and integration by parts, leads to

$$\pm \varepsilon^\gamma \int_{\Omega_\varepsilon} \frac{1}{2} (-\Delta \Phi_\varepsilon) (c_\varepsilon^\pm - \Lambda)_+^2 + \Lambda \varepsilon^\gamma (-\Delta \Phi_\varepsilon) (c_\varepsilon^\pm - \Lambda)_+ dx$$

Here the homogenous Neumann boundary condition for the electrostatic potential prevents the occurrence of boundary terms. Summation over \pm and inserting the Poisson equation leads to

$$\begin{aligned} \int_{\Omega_\varepsilon} \varepsilon^\gamma \left((c_\varepsilon^+ - c_\varepsilon^-) \frac{1}{2} (c_\varepsilon^+ - \Lambda)_+^2 - (c_\varepsilon^+ - c_\varepsilon^-) \frac{1}{2} (c_\varepsilon^- - \Lambda)_+^2 + \Lambda (c_\varepsilon^+ - c_\varepsilon^-) (c_\varepsilon^+ - \Lambda)_+ \right. \\ \left. - \Lambda (c_\varepsilon^+ - c_\varepsilon^-) (c_\varepsilon^- - \Lambda)_+ \right) dx =: \int_{\Omega_\varepsilon} T_D dx \end{aligned}$$

We now distinguish the following cases:

1. $c_\varepsilon^+ < \Lambda, c_\varepsilon^- < \Lambda$: $T_D = 0$
2. $c_\varepsilon^+ \geq \Lambda, c_\varepsilon^- < \Lambda$: $T_D = (c_\varepsilon^+ - c_\varepsilon^-) \frac{1}{2} (c_\varepsilon^+ - \Lambda)^2 + \Lambda (c_\varepsilon^+ - c_\varepsilon^-) (c_\varepsilon^+ - \Lambda) \geq 0$
3. $c_\varepsilon^+ < \Lambda, c_\varepsilon^- \geq \Lambda$: $T_D = -(c_\varepsilon^+ - c_\varepsilon^-) \frac{1}{2} (c_\varepsilon^- - \Lambda)^2 - \Lambda (c_\varepsilon^+ - c_\varepsilon^-) (c_\varepsilon^- - \Lambda) \geq 0$
4. $c_\varepsilon^+ \geq \Lambda, c_\varepsilon^- \geq \Lambda$:

$$\begin{aligned} T_D = \frac{1}{2} (c_\varepsilon^+ - \Lambda)^3 - \frac{1}{2} (c_\varepsilon^+ - \Lambda) (c_\varepsilon^- - \Lambda)^2 - \frac{1}{2} (c_\varepsilon^- - \Lambda) (c_\varepsilon^+ - \Lambda)^2 + \frac{1}{2} (c_\varepsilon^+ - \Lambda)^3 \\ + \Lambda (c_\varepsilon^+ - c_\varepsilon^-)^2 \geq 0 \end{aligned}$$

Here we used the identity $(c_\varepsilon^+ - c_\varepsilon^-) = (c_\varepsilon^+ - \Lambda) - (c_\varepsilon^- - \Lambda)$ and applied Young's inequality $(3, 3/2)$ which leads to a cancelation of all but the last term.

We now consider the reaction term $T_R := -(c_\varepsilon^+ - c_\varepsilon^-)(c_\varepsilon^+ - \Lambda)_+ + (c_\varepsilon^+ - c_\varepsilon^-)(c_\varepsilon^- - \Lambda)_+$ for the following cases:

1. $c_\varepsilon^+ < \Lambda, c_\varepsilon^- < \Lambda$: $T_R = 0$
2. $c_\varepsilon^+ \geq \Lambda, c_\varepsilon^- < \Lambda$: $T_R = -(c_\varepsilon^+ - c_\varepsilon^-)(c_\varepsilon^+ - \Lambda) \leq 0$
3. $c_\varepsilon^+ < \Lambda, c_\varepsilon^- \geq \Lambda$: $T_R = (c_\varepsilon^+ - c_\varepsilon^-)(c_\varepsilon^- - \Lambda) \leq 0$
4. $c_\varepsilon^+ \geq \Lambda, c_\varepsilon^- \geq \Lambda$: $T_R = -(c_\varepsilon^+ - c_\varepsilon^-)(c_\varepsilon^+ - \Lambda) + -(c_\varepsilon^+ - c_\varepsilon^-)(c_\varepsilon^- - \Lambda) = -(c_\varepsilon^+ - c_\varepsilon^-)^2 \leq 0$

Finally, since $T_D \geq 0$ and $T_R \leq 0$ we have

$$\begin{aligned} & \frac{1}{2} \frac{d}{dt} \left(\|(c_\varepsilon^+ - \Lambda)_+\|_{L^2(\Omega_\varepsilon)}^2 + \|(c_\varepsilon^- - \Lambda)_+\|_{L^2(\Omega_\varepsilon)}^2 \right) \\ & + \left(\|\nabla(c_\varepsilon^+ - \Lambda)_+\|_{L^2(\Omega_\varepsilon)}^2 + \|\nabla(c_\varepsilon^- - \Lambda)_+\|_{L^2(\Omega_\varepsilon)}^2 \right) \leq 0 \end{aligned}$$

Gronwall's lemma implies the statement of Theorem 3.4 since the initial concentrations are bounded from above by Λ according to Assumption 1.

In the following Theorem we state *a priori* estimates that are valid if we assume Neumann boundary data for the electrostatic potential on Γ_ε . This corresponds to a physical problem in which the surface charge of the porous medium is prescribed.

Theorem 3.5. *Let Assumption 1 and 2 be valid. The following a priori estimates hold in the case of pure Neumann boundary conditions for the electrostatic potential:*

$$\varepsilon^\alpha \|\Phi_\varepsilon\|_{L^2((0,T) \times \Omega_\varepsilon)} + \varepsilon^\alpha \|\nabla \Phi_\varepsilon\|_{L^2((0,T) \times \Omega_\varepsilon)} \leq C. \quad (7)$$

In the case $\beta - \alpha \geq 0$, it holds

$$\|v_\varepsilon\|_{L^2((0,T) \times \Omega_\varepsilon)} + \varepsilon \|\nabla v_\varepsilon\|_{L^2((0,T) \times \Omega_\varepsilon)} \leq C. \quad (8)$$

If additionally $\gamma - \alpha \geq 0$ is fulfilled, it holds

$$\begin{aligned} & \max_{0 \leq t \leq T} \|c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)} + \max_{0 \leq t \leq T} \|c_\varepsilon^+\|_{L^2(\Omega_\varepsilon)} + \|\nabla c_\varepsilon^-\|_{L^2((0,T) \times \Omega_\varepsilon)} + \|\nabla c_\varepsilon^+\|_{L^2((0,T) \times \Omega_\varepsilon)} \\ & + \|\partial_t c_\varepsilon^+\|_{L^2(0,T; (H^1(\Omega_\varepsilon))')} + \|\partial_t c_\varepsilon^-\|_{L^2(0,T; (H^1(\Omega_\varepsilon))')} \leq C, \end{aligned} \quad (9)$$

In (7), (8) and (9), $C \in \mathbb{R}_+$ is a constant independent of ε .

PROOF. To derive the *a priori* estimates we test (5c) with the potential Φ_ε which leads to

$$\begin{aligned} \varepsilon^\alpha \|\nabla \Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)}^2 & \leq \varepsilon \|\sigma\|_{L^2(\Gamma_\varepsilon)} \|\Phi_\varepsilon\|_{L^2(\Gamma_\varepsilon)} + \|c_\varepsilon^+ - c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)} \|\Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)} \\ & \leq \sqrt{\varepsilon} \|\sigma\|_{L^2(\Gamma_\varepsilon)} C (\|\Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)} + \varepsilon \|\nabla \Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)}) + \|c_\varepsilon^+ - c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)} \|\nabla \Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)} \\ & \leq C (\|\sigma\|_{L^2(\Gamma_\varepsilon)} + \|c_\varepsilon^+ - c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)}) \|\nabla \Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)}. \end{aligned}$$

Here we used $\varepsilon \|\Phi_\varepsilon\|_{L^2(\Gamma_\varepsilon)}^2 \leq C \left(\|\Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)}^2 + \varepsilon^2 \|\nabla \Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)}^2 \right)$ with some constant C independent of ε , see [13] Lemma 3, Poincaré's inequality for functions with zero mean value (cf. 2) and $\varepsilon < 1$. This results in

$$\varepsilon^\alpha \|\nabla \Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)} \leq C \left(\|\sigma\|_{L^2(\Gamma_\varepsilon)} + \|c_\varepsilon^+ - c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)} \right) \leq C,$$

since σ is constant and the concentration fields c_ε^\pm are bounded uniformly in ε , see Theorem 3.4. Using once again Poincaré's inequality leads directly to statement (7) after integration with respect to time. The constant C remains bounded ε -independently due to Theorem 3.4 and Assumption 1.

We test (5a) with the velocity field v_ε and apply Poincaré's inequality for functions with zero boundary values, i. e. $\|\varphi_\varepsilon\|_2 \leq C_P \varepsilon \|\nabla \varphi_\varepsilon\|_2$ with some constant C_P independent of ε , see [12], page 52. This leads due to the incompressibility of v_ε and the ε -independent boundedness of c_ε^\pm according to Theorem 3.4 to

$$\varepsilon^2 \|\nabla v_\varepsilon\|_{L^2(\Omega_\varepsilon)}^2 \leq \varepsilon^\beta 2\Lambda \|\nabla \Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)} \|v_\varepsilon\|_{L^2(\Omega_\varepsilon)} \leq \varepsilon^\beta C \|\nabla \Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)} \varepsilon \|\nabla v_\varepsilon\|_{L^2(\Omega_\varepsilon)}$$

This results in

$$\varepsilon \|\nabla v_\varepsilon\|_{L^2(\Omega_\varepsilon)} \leq \varepsilon^\beta C \|\nabla \Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)} \leq C,$$

if $\beta - \alpha \geq 0$, since the right hand side is bounded independently of ε due to the estimates derived for the electrostatic potential. Using once again Poincaré's inequality leads directly to statement (8) after integration with respect to time and the constant C remains bounded ε -independently.

In Theorem 3.4 we have already shown that c_ε^+ and c_ε^- are bounded by Λ uniformly in ε . We test the Nernst-Planck equation (5d) with $\varphi_3 = c_\varepsilon^\pm$ to obtain an energy estimate. This allows to bound also the gradient of the concentration fields.

$$\begin{aligned} & \frac{1}{2} \frac{d}{dt} \|c_\varepsilon^\pm\|_{L^2(\Omega_\varepsilon)}^2 + \|\nabla c_\varepsilon^\pm\|_{L^2(\Omega_\varepsilon)}^2 \\ & \leq \int_{\Omega_\varepsilon} |\varepsilon^\gamma c_\varepsilon^\pm \nabla \Phi_\varepsilon \cdot \nabla c_\varepsilon^\pm| dx + \int_{\Omega_\varepsilon} R_\varepsilon^\pm c_\varepsilon^\pm dx \leq \Lambda \varepsilon^\gamma \|\nabla \Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)} \|\nabla c_\varepsilon^\pm\|_{L^2(\Omega_\varepsilon)} + \int_{\Omega_\varepsilon} R_\varepsilon^\pm c_\varepsilon^\pm dx \\ & \leq \varepsilon^{2\gamma-2\alpha} C_\delta \left(\|\sigma\|_{L^2(\Gamma_\varepsilon)}^2 + \|c_\varepsilon^+ - c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)}^2 \right) + \delta \|\nabla c_\varepsilon^\pm\|_{L^2(\Omega_\varepsilon)}^2 + \int_{\Omega_\varepsilon} R_\varepsilon^\pm c_\varepsilon^\pm dx \end{aligned}$$

Here we used the estimate for the electrostatic potential derived above and that the velocity term cancels due to incompressibility of the fluid and the no slip boundary condition and Young's inequality. Summation over \pm , sorption with $\delta < 1/2$ and estimation of the reaction terms via $-(c_\varepsilon^+ - c_\varepsilon^-)c_\varepsilon^+ + (c_\varepsilon^+ - c_\varepsilon^-)c_\varepsilon^- \leq -(c_\varepsilon^+ - c_\varepsilon^-)^2 \leq 0$ finally leads to

$$\begin{aligned} & \frac{1}{2} \frac{d}{dt} \left(\|c_\varepsilon^+\|_{L^2(\Omega_\varepsilon)}^2 + \|c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)}^2 \right) + \frac{1}{2} \left(\|\nabla c_\varepsilon^+\|_{L^2(\Omega_\varepsilon)}^2 + \|\nabla c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)}^2 \right) \\ & \leq \varepsilon^{2\gamma-2\alpha} C_\delta \left(\|\sigma\|_{L^2(\Gamma_\varepsilon)}^2 + \|c_\varepsilon^+\|_{L^2(\Omega_\varepsilon)}^2 + \|c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)}^2 \right) \end{aligned}$$

Integration with respect to time gives an uniform estimate of the gradient if $\gamma - \alpha \geq 0$ since σ is constant and the concentration fields are bounded independently of ε .

To conclude the proof of Theorem 3.5, we still need to derive estimates for the time derivatives $\partial_t c_\varepsilon^\pm$ of the concentration fields. By the definition of the $(H^1)'$ norm and by equations (5d), we obtain

$$\begin{aligned} \|\partial_t c_\varepsilon^\pm\|_{(H^1(\Omega_\varepsilon))'} &= \sup_{\varphi \in H^1(\Omega_\varepsilon), \|\varphi\|_{H^1(\Omega_\varepsilon)} \leq 1} \langle \partial_t c_\varepsilon^\pm, \varphi \rangle_{(H^1)', H^1} \\ &\leq \sup_{\varphi \in H^1(\Omega_\varepsilon), \|\varphi\|_{H^1(\Omega_\varepsilon)} \leq 1} \left((\|c_\varepsilon^+ - c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)} + \Lambda \|v_\varepsilon - \varepsilon^\gamma \nabla \Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)} + \|\nabla c_\varepsilon^\pm\|_{L^2(\Omega_\varepsilon)}) \|\varphi\|_{H^1(\Omega_\varepsilon)} \right) \\ &\leq \|c_\varepsilon^+\|_{L^2(\Omega_\varepsilon)} + \|c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)} + \Lambda \|v_\varepsilon\|_{L^2(\Omega_\varepsilon)} + \Lambda \varepsilon^{\gamma-\alpha} \varepsilon^\alpha \|\nabla \Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)} + \|\nabla c_\varepsilon^\pm\|_{L^2(\Omega_\varepsilon)} \leq C, \end{aligned}$$

if $\gamma - \alpha \geq 0$ due to the uniform estimates for the gradient of the concentration and the potential derived above, respectively. Integration with respect to time therefore yields the last statement of Theorem 3.5.

In the following Theorem we state *a priori* estimates that are valid if we assume Dirichlet boundary data for the electrostatic potential on Γ_ε . This corresponds to a physical problem in which the surface potential of the porous medium is prescribed. In application in the geosciences this boundary condition is related to the specification of the so called ζ potential. We define the transformed electrostatic potential $\Phi_\varepsilon^{\text{hom}} := \Phi_\varepsilon - \Phi_D$. Since Φ_D is a constant according to Assumption 1, $\Phi_\varepsilon^{\text{hom}}$ fulfills the following set of equations:

$$-\varepsilon^\alpha \Delta \Phi_\varepsilon^{\text{hom}} = (c_\varepsilon^+ - c_\varepsilon^-) \quad \text{in } (0, T) \times \Omega_\varepsilon, \quad (10a)$$

$$\Phi_\varepsilon^{\text{hom}} = 0 \quad \text{in } (0, T) \times \Gamma_\varepsilon, \quad (10b)$$

$$\varepsilon^\alpha \nabla \Phi_\varepsilon^{\text{hom}} \cdot \nu = 0 \quad \text{in } (0, T) \times \partial\Omega. \quad (10c)$$

Theorem 3.6. *Let Assumption 1 be valid. The following a priori estimates hold in the case of Dirichlet boundary conditions on Γ_ε for the electrostatic potential*

$$\varepsilon^{\alpha-2} \|\Phi_\varepsilon^{\text{hom}}\|_{L^2((0,T) \times \Omega_\varepsilon)} + \varepsilon^{\alpha-1} \|\nabla \Phi_\varepsilon^{\text{hom}}\|_{L^2((0,T) \times \Omega_\varepsilon)} \leq C. \quad (11)$$

In the case $\beta - \alpha + 1 \geq 0$, it holds

$$\|v_\varepsilon\|_{L^2((0,T) \times \Omega_\varepsilon)} + \varepsilon \|\nabla v_\varepsilon\|_{L^2((0,T) \times \Omega_\varepsilon)} \leq C. \quad (12)$$

In the case $\gamma - \alpha + 1 \geq 0$, it holds

$$\begin{aligned} \max_{0 \leq t \leq T} \|c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)} + \max_{0 \leq t \leq T} \|c_\varepsilon^+\|_{L^2(\Omega_\varepsilon)} + \|\nabla c_\varepsilon^-\|_{L^2((0,T) \times \Omega_\varepsilon)} + \|\nabla c_\varepsilon^+\|_{L^2((0,T) \times \Omega_\varepsilon)} \\ + \|\partial_t c_\varepsilon^+\|_{L^2(0,T; (H^1(\Omega_\varepsilon))')} + \|\partial_t c_\varepsilon^-\|_{L^2(0,T; (H^1(\Omega_\varepsilon))')} \leq C. \end{aligned} \quad (13)$$

In (11), (12) and (13), $C \in \mathbb{R}_+$ is a constant independent of ε .

PROOF. We test equation (10a) with the translated potential $\Phi_\varepsilon^{\text{hom}}$ and use Poincaré's inequality for zero boundary data, see [12]. This leads to

$$\varepsilon^\alpha \|\nabla \Phi_\varepsilon^{\text{hom}}\|_{L^2(\Omega_\varepsilon)}^2 \leq \|c_\varepsilon^+ - c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)} \|\Phi_\varepsilon^{\text{hom}}\|_{L^2(\Omega_\varepsilon)} \leq \|c_\varepsilon^+ - c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)} \varepsilon C_P \|\nabla \Phi_\varepsilon^{\text{hom}}\|_{L^2(\Omega_\varepsilon)},$$

which results in

$$\varepsilon^{\alpha-1} \|\nabla \Phi_\varepsilon^{\text{hom}}\|_{L^2(\Omega_\varepsilon)} \leq C_P \|c_\varepsilon^+ - c_\varepsilon^-\|_{L^2(\Omega_\varepsilon)} \leq C$$

Here we have used the boundedness of the concentration fields c_ε^\pm provided by Theorem 3.4 with C being a constant independent of ε . Using again Poincaré's inequality leads to

$$\varepsilon^{\alpha-2} \|\Phi_\varepsilon^{\text{hom}}\|_{L^2(\Omega_\varepsilon)} \leq C$$

Altogether, we obtain the statement (11) directly after integration with respect to time. By means of Theorem 3.4, the constant C remains bounded ε -independently.

The rest of the statement in Theorem 3.6 follows analogously to the proof of Theorem 3.5 since due to the definition of the translated electrostatic potential and Theorem 3.6, it holds $\varepsilon^{\alpha-1} \|\nabla \Phi_\varepsilon\|_{L^2(\Omega_\varepsilon)} = \varepsilon^{\alpha-1} \|\nabla \Phi_\varepsilon^{\text{hom}}\|_{L^2(\Omega_\varepsilon)} \leq C$.

The (stationary) system consisting of (1a) and (2a) without convective term is well known as drift-diffusion model or van-Roosbroeck system in the theory of semiconductor devices [26]. Analytical investigations treating existence and uniqueness of solutions of this system can be found in [19] and [26]. Extensions of the system (1a) and (2a) to the Navier-Stokes equations have been considered analytically, for instance, in [26], [27]. The results proven there can be carried over to system (4) and the following Theorem holds true:

Theorem 3.7. *Let Assumption 2 and 1 be valid. For each $\varepsilon > 0$ there exists a unique weak solution of Problem P_ε in the sense of Definition 3.1.*

4. Upscaling of Problem P_ε

This section is the bulk of the paper. Here we pass rigorously to the limit $\varepsilon \rightarrow 0$ in the non-stationary pore scale model P_ε for both the Neumann and Dirichlet case and different choices of scaling (α, β, γ) . For this aim we apply the method of two-scale convergence which has been introduced by Nguetseng in [23] and further developed by Allaire in [1]. An introduction to this topic and the application of this method to basic model equations can be found, for example, in [7] and [12]. For the reader's convenience, we state the definition of two-scale convergence as well as the basic compactness result for functions defined on a time-space cylinder, see, e.g., [18] and [22]:

Definition 4.1. *A sequence of functions $\{\varphi_\varepsilon\}$ in $L^2((0, T) \times \Omega)$ is said to two-scale converge to a limit φ_0 belonging to $L^2((0, T) \times \Omega \times Y)$ if, for any function ψ in $D((0, T) \times \Omega; C_{\text{per}}^\infty(Y))$, we have*

$$\lim_{\varepsilon \rightarrow 0} \int_0^T \int_\Omega \varphi_\varepsilon(t, x) \psi\left(t, x, \frac{x}{\varepsilon}\right) dx dt = \int_0^T \int_{\Omega \times Y} \varphi_0(t, x, y) \psi(t, x, y) dy dx dt.$$

In short notation we write $\varphi_\varepsilon \xrightarrow{2} \varphi_0$.

A sequence of functions $\{\varphi_\varepsilon\}$ in $L^2((0, T) \times \Gamma_\varepsilon)$ is said to two-scale converge to a limit φ_0 belonging to $L^2((0, T) \times \Omega \times \Gamma)$ if, for any function ψ in $D((0, T) \times \Omega; C_{\text{per}}^\infty(\Gamma))$, we have

$$\lim_{\varepsilon \rightarrow 0} \varepsilon \int_0^T \int_{\Gamma_\varepsilon} \varphi_\varepsilon(t, x) \psi\left(t, x, \frac{x}{\varepsilon}\right) dx dt = \int_0^T \int_{\Omega \times \Gamma} \varphi_0(t, x, y) \psi(t, x, y) dy dx dt.$$

Here $D((0, T) \times \Omega; C_{\text{per}}^\infty(Y))$ and $D((0, T) \times \Omega; C_{\text{per}}^\infty(\Gamma))$ denote the function space of infinitely smooth functions having compact support in $(0, T) \times \Omega$ with values in the space of infinitely differentiable functions that are periodic in Y and Γ , respectively. The following compactness result allows to extract converging subsequences from bounded sequences and therefore yields the possibility to pass to the two-scale limit provided that suitable *a priori* estimates can be shown.

Theorem 4.2.

1. Let $\{\varphi_\varepsilon\}$ be a bounded sequence in $L^2((0, T) \times \Omega)$. Then there exists a function φ_0 in $L^2((0, T) \times \Omega \times Y)$ such that, up to a subsequence, φ_ε two-scale converges to φ_0 .
2. Let $\{\varphi_\varepsilon\}$ be a bounded sequence in $L^2(0, T; H^1(\Omega))$. Then there exist functions φ_0 in $L^2(0, T; H^1(\Omega))$ and φ_1 in $L^2((0, T) \times \Omega; H_{\text{per}}^1(Y))$ such that, up to a subsequence, φ_ε two-scale converges to φ_0 and $\nabla \varphi_\varepsilon$ two-scale converges to $\nabla_x \varphi_0 + \nabla_y \varphi_1$.
3. Let $\{\varphi_\varepsilon\}$ and $\{\varepsilon \nabla \varphi_\varepsilon\}$ be bounded sequence in $L^2((0, T) \times \Omega)$. Then there exists a function φ_0 in $L^2((0, T) \times \Omega; H_{\text{per}}^1(Y))$ such that, up to a subsequence, φ_ε and $\varepsilon \nabla \varphi_\varepsilon$ two-scale converge to φ_0 and $\nabla_y \varphi_0$, respectively.
4. Let $\{\varphi_\varepsilon\}$ be a bounded sequence in $L^2((0, T) \times \Gamma_\varepsilon)$. Then there exists a function φ_0 in $L^2((0, T) \times \Omega \times \Gamma)$ such that, up to a subsequence, φ_ε two-scale converges to φ_0 .

PROOF. For a proof of the time independent case we refer e. g. to [1], [22] and [23]. The proof can easily be carried over to the time dependent case.

One difficulty is that the *a priori* estimates that have been derived in Theorem 3.5 and Theorem 3.6 are at first only valid within the perforated domain Ω_ε . Therefore an extension of the functions $v_\varepsilon, \nabla v_\varepsilon, p_\varepsilon, \Phi_\varepsilon, \nabla \Phi_\varepsilon, c_\varepsilon^\pm, \partial_t c_\varepsilon^\pm, \nabla c_\varepsilon^\pm$ is necessary, such that appropriate *a priori* estimates can be extended and that the limits for $\varepsilon \rightarrow 0$ can be identified in function spaces on Ω . This procedure is quite standard and we refer to [1], [8], [9], [12] and [13] for the strategy and the proof of the following

Theorem 4.3. For the concentration fields c_ε^\pm we apply a linear extensions operator $E \in \mathcal{L}(H^1(\Omega_\varepsilon), H^1(\Omega))$, such that

$$\|E(c_\varepsilon^\pm)\|_{H^1(\Omega)}^2 := \|E(c_\varepsilon^\pm)\|_{L^2(\Omega)}^2 + \|\nabla E(c_\varepsilon^\pm)\|_{L^2(\Omega)}^2 \leq C \|c_\varepsilon^\pm\|_{H^1(\Omega_\varepsilon)}^2$$

is valid.

The pressure field p_ε is extended via

$$E(p_\varepsilon) := \begin{cases} p_\varepsilon & \text{in } \Omega_\varepsilon, \\ \frac{1}{|Y_{l,i}^\varepsilon|} \int_{Y_{l,i}^\varepsilon} p_\varepsilon dy & \text{in each } Y_{s,i}^\varepsilon, \end{cases}$$

and the following uniform a priori estimate holds if we assume zero mean value in Ω :

$$\|E(p_\varepsilon)\|_{L^2((0,T) \times \Omega)} \leq C.$$

The other variables are extended by zero into Ω . Then Ω_ε can be replaced by Ω in the a priori estimates from Theorem 3.5 and Theorem 3.6.

However, for the ease of presentation we suppress the notation of the extensions and write again φ_ε instead of $E(\varphi_\varepsilon)$.

In the next two subsections we consider the homogenization of system (4) for both the Neumann and Dirichlet case via two-scale convergence. The statements on the two-scale limits of the extended functions and on the derivation of the macroscopic limit equations are deduced using the a priori estimates in Theorem 3.5 and Theorem 3.6. Special attention is paid to the coupling via the electrostatic interaction and the influence of the ranges of scaling on the limit equations. We first state the following

Definition 4.4. We define the averaged macroscopic permittivity and diffusion tensor by

$$D_{ij} := \int_{Y_l} (\delta_{ij} + \partial_{y_i} \varphi_j(y)) dy, \quad (14)$$

where φ_j are solutions of the following family of cell problems ($j = 1, \dots, n$)

$$-\Delta_y \varphi_j(y) = 0 \quad \text{in } Y_l, \quad (15a)$$

$$\nabla_y \varphi_j(y) \cdot \nu = -e_j \cdot \nu \quad \text{on } \Gamma, \quad (15b)$$

$$\varphi_j \quad \text{periodic in } y. \quad (15c)$$

We define the averaged macroscopic permeability tensor by

$$K_{ij} = \int_{Y_l} w_j^i dy, \quad (16)$$

where w_j are solutions of the following family of cell problems ($j = 1, \dots, n$)

$$-\Delta_y w_j + \nabla_y \pi_j = e_j \quad \text{in } Y_l \quad (17a)$$

$$\nabla_y \cdot w_j = 0 \quad \text{in } \Omega \times Y_l \quad (17b)$$

$$w_j = 0 \quad \text{in } Y_s \quad (17c)$$

$$w_j \quad \text{periodic in } y \quad (17d)$$

Furthermore, we define the following cell problem

$$-\Delta_y \varphi(y) = 1 \quad \text{in } Y_l, \quad (18a)$$

$$\varphi(y) = 0 \quad \text{on } \Gamma, \quad (18b)$$

$$\varphi \quad \text{periodic in } y. \quad (18c)$$

4.1. Neumann boundary condition

We define $\tilde{\Phi}_\varepsilon := \varepsilon^\alpha \Phi_\varepsilon$.

4.1.1. Homogenized Limit Problems for Poisson's Equation

Theorem 4.5. *Let the a priori estimates of Theorem 3.5 be valid. Then the following two-scale limits can be identified for the electrostatic potential $\tilde{\Phi}_\varepsilon$ and its gradient $\nabla \tilde{\Phi}_\varepsilon$: There exist functions $\tilde{\Phi}_0 \in L^2(0, T; H^1(\Omega))$ and $\tilde{\Phi}_1 \in L^2((0, T) \times \Omega; H_{per}^1(Y))$ such that, up to a subsequence,*

$$\begin{aligned} \tilde{\Phi}_\varepsilon(t, x) &\xrightarrow{2} \tilde{\Phi}_0(t, x), \\ \nabla \tilde{\Phi}_\varepsilon(t, x) &\xrightarrow{2} \nabla_x \tilde{\Phi}_0(t, x) + \nabla_y \tilde{\Phi}_1(t, x, y). \end{aligned}$$

PROOF. We consider the estimate (7) in Theorem 3.5 which implies

$$\|\tilde{\Phi}_\varepsilon\|_{L^2(\Omega)} + \|\nabla \tilde{\Phi}_\varepsilon\|_{L^2(\Omega)} \leq C.$$

Theorem 4.2 ensures the existence of the two-scale limit functions.

Theorem 4.6. *Let $(v_\varepsilon, p_\varepsilon, \Phi_\varepsilon, c_\varepsilon^+, c_\varepsilon^-)$ be a weak solution of Problem P_ε in the sense of Definition 3.1. Assume that c_ε^\pm converge strongly to c_0^\pm in $L^2((0, T) \times \Omega)$. Then the two-scale limits of $\tilde{\Phi}_\varepsilon$ due to Theorem 4.5 satisfy the following equations:*

$$\begin{aligned} -\nabla_x \cdot (D \nabla_x \tilde{\Phi}_0(t, x)) - \bar{\sigma}_0 &= |Y_l| (c_0^+(t, x) - c_0^-(t, x)) \quad \text{in } (0, T) \times \Omega, \\ D \nabla_x \tilde{\Phi}_0(t, x) \cdot \nu &= 0 \quad \text{on } (0, T) \times \partial \Omega. \end{aligned}$$

PROOF. To prove Theorem 4.6 we test Poisson's equation (5c) with test function $(\psi_0(t, x) + \varepsilon \psi_1(t, x, \frac{x}{\varepsilon}))$ which leads to

$$\begin{aligned} &\int_0^T \int_\Omega \nabla \tilde{\Phi}_\varepsilon(t, x) \cdot \nabla \left(\psi_0(t, x) + \varepsilon \psi_1 \left(t, x, \frac{x}{\varepsilon} \right) \right) dx dt \\ &\quad - \int_0^T \int_{\Gamma_\varepsilon} \varepsilon \sigma \left(\psi_0(t, x) + \varepsilon \psi_1 \left(t, x, \frac{x}{\varepsilon} \right) \right) dx dt \\ &= \int_0^T \int_\Omega \chi_\varepsilon(x) (c_\varepsilon^+(t, x) - c_\varepsilon^-(t, x)) \left(\psi_0(t, x) + \varepsilon \psi_1 \left(t, x, \frac{x}{\varepsilon} \right) \right) dx dt. \end{aligned}$$

We then pass to the two-scale limit $\varepsilon \rightarrow 0$ using the properties we have stated in Theorem 4.5:

$$\begin{aligned} &\int_0^T \int_{\Omega \times Y_l} \chi(y) \left(\nabla_x \tilde{\Phi}_0(t, x) + \nabla_y \tilde{\Phi}_1(t, x, y) \right) \cdot (\nabla_x \psi_0(t, x) + \nabla_y \psi_1(t, x, y)) dy dx dt \\ &\quad - \int_0^T \int_{\Omega \times \Gamma} \sigma_0 \psi_0(t, x) do_y dx dt \\ &= \int_0^T \int_{\Omega \times Y_l} \chi(y) (c_0^+(t, x) - c_0^-(t, x)) \psi_0(t, x) dy dx dt \end{aligned}$$

Now, we choose $\psi_0(t, x) = 0$, which leads, after integration by parts with respect to y , to

$$\begin{aligned} -\nabla_y \cdot \left(\nabla_x \tilde{\Phi}_0(t, x) + \nabla_y \tilde{\Phi}_1(t, x, y) \right) &= 0 && \text{in } (0, T) \times \Omega \times Y_l, \\ \left(\nabla_x \tilde{\Phi}_0(t, x) + \nabla_y \tilde{\Phi}_1(t, x, y) \right) \cdot \nu &= 0 && \text{on } (0, T) \times \Omega \times \Gamma, \\ \tilde{\Phi}_1(t, x, y) &&& \text{periodic in } y \end{aligned}$$

and, therefore, also to

$$-\Delta_y \tilde{\Phi}_1(t, x, y) = 0 \quad \text{in } (0, T) \times \Omega \times Y_l, \quad (19a)$$

$$\nabla_y \tilde{\Phi}_1(t, x, y) \cdot \nu = -\nabla_x \tilde{\Phi}_0(t, x) \cdot \nu \quad \text{on } (0, T) \times \Omega \times \Gamma, \quad (19b)$$

$$\tilde{\Phi}_1(t, x, y) \quad \text{periodic in } y. \quad (19c)$$

Due to the linearity of the equation, we can deduce the following representation of $\tilde{\Phi}_1$:

$$\tilde{\Phi}_1(t, x, y) = \sum_j \varphi_j(y) \partial_{x_j} \tilde{\Phi}_0(t, x) \quad (20)$$

with φ_j being solutions of the standard family of $j = 1, \dots, n$ cell problems (15).

On the other hand, if we choose $\psi_1(t, x, y) = 0$, we may read off, after integration by parts with respect to x , the strong formulation for $\tilde{\Phi}_0$:

$$\begin{aligned} \nabla_x \cdot \left(\int_{Y_l} \nabla_x \tilde{\Phi}_0(t, x) + \nabla_y \tilde{\Phi}_1(t, x, y) dy \right) - \int_{\Gamma} \sigma_0 d\sigma_y &= |Y_l| (c_0^+(t, x) - c_0^-(t, x)) \quad \text{in } (0, T) \times \Omega, \\ \left(\int_{Y_l} \nabla_x \tilde{\Phi}_0(t, x) + \nabla_y \tilde{\Phi}_1(t, x, y) dy \right) \cdot \nu &= 0 \quad \text{on } (0, T) \times \partial\Omega. \end{aligned}$$

Inserting the representation (20) of $\tilde{\Phi}_1$ yields

$$\begin{aligned} \nabla_x \cdot \left(D \nabla_x \tilde{\Phi}_0(t, x) \right) - \bar{\sigma}_0 &= |Y_l| (c_0^+(t, x) - c_0^-(t, x)) \quad \text{in } \Omega, \\ D \nabla_x \tilde{\Phi}_0(t, x) \cdot \nu &= 0 \quad \text{on } \partial\Omega \end{aligned}$$

with diffusion tensor D being defined in (14) and $\bar{\sigma}_0 := \int_{\Gamma} \sigma_0 d\sigma_y$.

Remark 4 (Modeling of $\tilde{\Phi}_0$). In the case $\alpha = 0$, it follows $\tilde{\Phi}_\varepsilon = \Phi_\varepsilon$. Therefore, we have an macroscopic equation for the leading order potential $\tilde{\Phi}_0$ which is directly coupled to the macroscopic concentrations c_0^\pm . The case $\alpha < 0$ implies that $\tilde{\Phi}_\varepsilon$ and $\nabla \tilde{\Phi}_\varepsilon$ converge to zero. However, for any α an effective equation can be derived for the limit $\tilde{\Phi}_0$ of $\tilde{\Phi}_\varepsilon$.

4.1.2. Homogenized Limit Problems for Stokes' Equation

Theorem 4.7. *Let the a priori estimates of Theorem 3.5 be valid, i.e. especially $\beta \geq \alpha$. Then the following two-scale limits can be identified for the velocity field v_ε and the gradient $\varepsilon \nabla v_\varepsilon$: There exists $v_0 \in L^2((0, T) \times \Omega; H_{per}^1(Y))$ such that, up to a subsequence,*

$$\begin{aligned} v_\varepsilon(t, x) &\xrightarrow{2} v_0(t, x, y), \\ \varepsilon \nabla v_\varepsilon(t, x) &\xrightarrow{2} \nabla_y v_0(t, x, y). \end{aligned}$$

PROOF. We consider the estimate (8) in Theorem 3.5 which implies due to Theorem 4.2 the existence of the two-scale limit functions.

The convergence for p_ε are standard, see [12] and we follow directly the procedure there including the right hand side which is due to the electrostatic interaction. Depending on the choice of the scale range, this possibly leads to a coupling of the flow with the electrostatic potential and the concentration fields as stated in the following

Theorem 4.8. *Let $(v_\varepsilon, p_\varepsilon, \Phi_\varepsilon, c_\varepsilon^+, c_\varepsilon^-)$ be a weak solution of Problem P_ε in the sense of Definition 3.1. Assume that c_ε^\pm converge strongly to c_0^\pm in $L^2((0, T) \times \Omega)$.*

For $\beta \geq \alpha$ the two-scale limit of v_ε due to Theorem 4.7 satisfies the following equations:

$$\begin{aligned} \bar{v}_0(t, x) &= -K \left(\nabla_x p_0(t, x) + \begin{cases} (c_0^+(t, x) - c_0^-(t, x)) \nabla_x \tilde{\Phi}_0(t, x), & \beta = \alpha \\ 0, & \beta > \alpha \end{cases} \right) \quad \text{in } (0, T) \times \Omega, \\ \nabla_x \cdot \bar{v}_0(t, x) &= 0 \quad \text{in } (0, T) \times \Omega. \end{aligned}$$

PROOF. Choose $\varepsilon \psi(t, x, \frac{x}{\varepsilon})$ as test function:

$$\begin{aligned} \int_0^T \int_\Omega \varepsilon \nabla v_\varepsilon(t, x) \cdot \varepsilon^2 \nabla \psi \left(t, x, \frac{x}{\varepsilon} \right) - p_\varepsilon(t, x) \varepsilon \nabla \cdot \psi \left(t, x, \frac{x}{\varepsilon} \right) dx dt \\ = \int_0^T \int_\Omega -\varepsilon^{\beta+1} (c_\varepsilon^+(t, x) - c_\varepsilon^-(t, x)) \nabla \Phi_\varepsilon(t, x) \psi \left(t, x, \frac{x}{\varepsilon} \right) dx dt. \end{aligned}$$

Passage to the limit leads to

$$\int_0^T \int_{\Omega \times Y} -p_0(t, x, y) \nabla_y \cdot \psi(t, x, y) dy dx dt = 0,$$

which gives $p_0(t, x, y) = p_0(t, x)$.

We define the space $V_\psi = \{\nabla_y \cdot \psi = 0, \nabla_x \cdot \int_{Y_l} \psi dy = 0, \psi = 0 \text{ on } (0, T) \times \Omega \times Y_s\}$ and choose $\psi(t, x, \frac{x}{\varepsilon}) \in V_\psi$ as test function:

$$\begin{aligned} \int_0^T \int_\Omega \varepsilon \nabla v_\varepsilon(t, x) \cdot \varepsilon \nabla \psi \left(t, x, \frac{x}{\varepsilon} \right) - p_\varepsilon(t, x) \nabla \cdot \psi \left(t, x, \frac{x}{\varepsilon} \right) dx \\ = \int_0^T \int_\Omega -\varepsilon^\beta (c_\varepsilon^+(t, x) - c_\varepsilon^-(t, x)) \nabla \Phi_\varepsilon(t, x) \psi \left(t, x, \frac{x}{\varepsilon} \right) dx \end{aligned}$$

Passage to the limit leads to

$$\int_0^T \int_{\Omega \times Y_l} \nabla_y v_0 \cdot \nabla_y \psi - p_0 \nabla_x \cdot \psi dy dx = \begin{cases} \int_0^T \int_{\Omega \times Y_l} -(c_0^+ - c_0^-) (\nabla_x \tilde{\Phi}_0 + \nabla_y \tilde{\Phi}_1) \psi dy dx, & \beta = \alpha \\ 0, & \beta > \alpha \end{cases}$$

Here we applied that $\psi \in V_\psi$, i.e. $\nabla_y \cdot \psi = 0$ holds. The property $p_0 = p_0(x)$ yields

$$\int_0^T \int_\Omega -p_0(t, x) \nabla_x \cdot \left(\int_{Y_l} \psi(t, x, y) dy \right) dx dt = 0$$

Integration by parts inserting the properties of the orthogonal of V_ψ and identification of the pressure p_0 as in [12] leads to

$$\begin{aligned}
-\Delta_y v_0 + \nabla_x p_0 + \nabla_y p_1 &= \begin{cases} -(c_0^+ - c_0^-)(\nabla_x \tilde{\Phi}_0 + \nabla_y \tilde{\Phi}_1), & \beta = \alpha \\ 0, & \beta > \alpha \end{cases} & \text{in } (0, T) \times \Omega \times Y_l \\
\nabla_y \cdot v_0 &= 0 & \text{in } (0, T) \times \Omega \times Y_l \\
\nabla_x \cdot \int_{Y_l} v_0 dy &= 0 & \text{in } (0, T) \times \Omega \\
\int_{Y_l} v_0 dy \cdot \nu &= 0 & \text{on } (0, T) \times \partial\Omega \\
v_0 &= 0 & \text{on } (0, T) \times \Omega \times Y_s
\end{aligned}$$

If $\beta = \alpha$, we define the modified pressure $\tilde{p}_1 = p_1 + (c_0^+ - c_0^-)\tilde{\Phi}_1$ in order to determine a macroscopic extended Darcy's Law. Due to the linearity of the equations v_0 can be represented as

$$v_0(t, x, y) = - \sum_j w_j(y) \left(\partial_{x_j} p_0(t, x) + \begin{cases} (c_0^+(t, x) - c_0^-(t, x)) \partial_{x_j} \tilde{\Phi}_0(t, x), & \beta = \alpha \\ 0, & \beta > \alpha \end{cases} \right)$$

with w_j being solutions of the cell problems (17). We define the averaged velocity field via

$$\bar{v}_0(t, x) = \int_{Y_l} v_0(t, x, y) dy. \quad (21)$$

which leads, after integration with respect to y , to

$$\begin{aligned}
\bar{v}_0(t, x) &= -K \left(\nabla_x p_0(t, x) + \begin{cases} (c_0^+(t, x) - c_0^-(t, x)) \nabla_x \tilde{\Phi}_0(t, x), & \beta = \alpha \\ 0, & \beta > \alpha \end{cases} \right) & \text{in } (0, T) \times \Omega \\
\nabla_x \cdot \bar{v}_0(t, x) &= 0 & \text{in } (0, T) \times \Omega
\end{aligned}$$

with the permeability tensor K being defined in (16).

Remark 5 (Modeling of \bar{v}_0). In the case $\beta = \alpha$, we derive an extended incompressible Darcy's law. Besides the pressure gradient, an additional forcing term occurs due to the electrostatic potential. In the case $\beta > \alpha$, the electrostatic potential has no influence on the macroscopic velocity, which is then determined by a standard Darcy's law.

4.1.3. Homogenized Limit Problems for the Nernst-Planck Equations

Theorem 4.9. *Let the estimates of Theorem 3.5 be valid. Then the following two-scale limits can be identified for the concentration fields c_ε^\pm and their gradients ∇c_ε^\pm in the case $\gamma - \alpha \geq 0$: There exist functions $c_0^\pm(t, x) \in L^2((0, T); H^1(\Omega))$ and $c_1(t, x, y) \in L^2((0, T) \times \Omega; H_{per}^1(Y))$ such that (up to a subsequence)*

$$\begin{aligned}
c_\varepsilon^\pm(t, x) &\rightarrow c_0^\pm(t, x), \\
\nabla c_\varepsilon^\pm(t, x) &\xrightarrow{2} \nabla_x c_0^\pm(t, x) + \nabla_y c_1^\pm(t, x, y).
\end{aligned}$$

PROOF. The statement of strong convergence holds true due to the extension of the concentration fields c_ε^\pm with the properties defined in Theorem 4.3 and Aubin-Lions compact embedding lemma.

Remark 6. The strong convergence of the concentrations c_ε^\pm in $L^2(0, T; L^2(\Omega))$ enables us to pass to the limit $\varepsilon \rightarrow 0$ also in the convective and drift term of the Nernst-Planck equations (5d).

Theorem 4.10. *Let $(v_\varepsilon, p_\varepsilon, \Phi_\varepsilon, c_\varepsilon^+, c_\varepsilon^-)$ be a weak solution of Problem P_ε in the sense of Definition 3.1. Assume that $\nabla \Phi_\varepsilon$ and v_ε two-scale converge as stated in Theorem 4.5 and Theorem 4.7, respectively.*

Then the two-scale limits of the concentrations as stated in Theorem 4.9 satisfy the following macroscopic limit equations:

$$\begin{aligned} & |Y_l| \partial_t c_0^\pm(t, x) + \nabla_x \cdot \left(\bar{v}_0(t, x) c_0^\pm(t, x) - D \nabla_x c_0^\pm(t, x) \pm \begin{cases} D c_0^\pm(t, x) \nabla_x \tilde{\Phi}_0(t, x), & \gamma = \alpha \\ 0, & \gamma > \alpha \end{cases} \right) \\ & \quad = |Y_l| R_0^\pm(c_0^+(t, x), c_0^-(t, x)) \text{ in } (0, T) \times \Omega, \\ & \left(\bar{v}_0(t, x) c_0^\pm(t, x) - D \nabla_x c_0^\pm(t, x) \pm \begin{cases} D c_0^\pm(t, x) \nabla_x \tilde{\Phi}_0(t, x), & \gamma = \alpha \\ 0, & \gamma > \alpha \end{cases} \right) \cdot \nu = 0 \text{ on } (0, T) \times \partial \Omega, \end{aligned}$$

PROOF. We choose $\varphi_{2,3} = \psi_0(t, x) + \varepsilon \psi_1(t, x, \frac{x}{\varepsilon})$ as test function in the Nernst-Planck equations (5d) and obtain:

$$\begin{aligned} & \int_0^T \int_\Omega -c_\varepsilon^\pm(t, x) \partial_t \left(\psi_0(t, x) + \varepsilon \psi_1 \left(t, x, \frac{x}{\varepsilon} \right) \right) + (-v_\varepsilon(t, x) c_\varepsilon^\pm(t, x) \\ & \quad + \nabla c_\varepsilon^\pm(t, x) \pm \varepsilon^\gamma c_\varepsilon^\pm(t, x) \nabla \Phi_\varepsilon(t, x)) \cdot \nabla \left(\psi_0(t, x) + \varepsilon \psi_1 \left(t, x, \frac{x}{\varepsilon} \right) \right) dx dt \\ & \quad = \int_0^T \int_\Omega R_\varepsilon^\pm(c_\varepsilon^+(t, x), c_\varepsilon^-(t, x)) \left(\psi_0(t, x) + \varepsilon \psi_1 \left(t, x, \frac{x}{\varepsilon} \right) \right) dx dt. \end{aligned}$$

Due to Theorem 4.9 and Assumption 1, we pass to the two-scale limit $\varepsilon \rightarrow 0$.

$$\begin{aligned} & \int_0^T \int_{\Omega \times Y_l} -c_0^\pm(t, x) \partial_t \psi_0(t, x) + \left(-v_0(t, x, y) c_0^\pm(t, x) + (\nabla c_0^\pm(t, x) + \nabla_y c_1^\pm(t, x, y)) \right. \\ & \quad \left. \pm \begin{cases} c_0^\pm(\nabla_x \tilde{\Phi}_0 + \nabla_y \tilde{\Phi}_1), & \gamma = \alpha \\ 0, & \gamma > \alpha \end{cases} \right) \cdot (\nabla_x \psi_0(t, x) + \nabla_y \psi_1(t, x, y)) dy dx dt \\ & \quad = \int_0^T \int_{\Omega \times Y_l} R_0^\pm(c_0^+(t, x), c_0^-(t, x)) \psi_0(t, x) dy dx dt. \end{aligned}$$

In the case $\gamma = \alpha$ we define $\tilde{c}_1^\pm := c_1^\pm \pm c_0^\pm \tilde{\Phi}_1$. We choose $\psi_0 \equiv 0$, which leads, after integration by parts with respect to y , to

$$\begin{aligned} & -\Delta_y c_1^\pm(t, x, y) = 0 && \text{in } (0, T) \times \Omega \times Y_l, \\ & \nabla_y c_1^\pm(t, x, y) \cdot \nu = -\nabla_x c_0^\pm(t, x) \mp \begin{cases} c_0^\pm(t, x) \nabla_x \tilde{\Phi}_0(t, x) \cdot \nu, & \gamma = \alpha \\ 0, & \gamma > \alpha \end{cases} && \text{on } (0, T) \times \Omega \times \Gamma, \\ & c_1^\pm(t, x, y) && \text{periodic in } y. \end{aligned}$$

Due to the linearity of the equation, we deduce the following representations for c_1^\pm :

$$c_1^\pm(t, x, y) = \sum_j \varphi_j(y) \partial_{x_j} c_0^\pm(t, x) \pm \begin{cases} c_0^\pm \partial_{x_j} \tilde{\Phi}_0, & \gamma = \alpha \\ 0, & \gamma > \alpha \end{cases} \quad (22)$$

where φ_j is the solution of the standard cell problem (15).

On the other hand, if we choose $\psi_1(t, x, y) = 0$, we read off the strong formulation for c_0^\pm , after integration by parts with respect to x , and after inserting the representation (22) of c_1^\pm :

$$\begin{aligned} & |Y_l| \partial_t c_0^\pm(t, x) + \nabla_x \cdot \left(\bar{v}_0(t, x) c_0^\pm(t, x) - D \nabla_x c_0^\pm(t, x) \pm \begin{cases} D c_0^\pm \nabla_x \tilde{\Phi}_0, & \gamma = \alpha \\ 0, & \gamma > \alpha \end{cases} \right) \\ & = |Y_l| R_0^\pm(c_0^+(t, x), c_0^-(t, x)) \text{ in } (0, T) \times \Omega, \\ & \left(\bar{v}_0(t, x) c_0^\pm(t, x) - D \nabla_x c_0^\pm(t, x) \pm \begin{cases} D c_0^\pm \nabla_x \tilde{\Phi}_0, & \gamma = \alpha \\ 0, & \gamma > \alpha \end{cases} \right) \cdot \nu = 0 \text{ on } (0, T) \times \partial\Omega, \end{aligned}$$

with D and \bar{v}_0 being defined in (14) and (21), respectively.

Remark 7 (Modeling of c_0^\pm). Mainly two different types of limit equations arise for the macroscopic problem description. In the case $\gamma = \alpha$, the transport of the concentrations is given by Nernst-Planck equations. Thereby the limit $\tilde{\Phi}_0$ of the electrostatic potential and \bar{v}_0 are given in Theorem 4.5 and Theorem 4.7. The upscaling procedure then yields a fully coupled system of partial differential equation. In the case $\gamma > \alpha$, the electrostatic potential has no direct influence on the macroscopic concentrations. The equations for the concentrations simplify to a convection-diffusion-reaction equation. Depending on the choice of β , the effective equations might be coupled only in one direction.

The two families of cell problems (15) and (15) yield the same solutions and therefore the same macroscopic coefficients (up to the constant parameters that we have suppressed for the ease of presentation).

4.2. Dirichlet boundary condition

4.2.1. Homogenized Limit Problems for Poisson's Equation

We define $\tilde{\Phi}_\varepsilon := \varepsilon^{\alpha-2} \Phi_\varepsilon^{\text{hom}}$ which fulfills the following set of equations:

$$-\varepsilon^2 \Delta \tilde{\Phi}_\varepsilon = c_\varepsilon^+ - c_\varepsilon^- \quad \text{in } (0, T) \times \Omega_\varepsilon, \quad (23)$$

$$\tilde{\Phi}_\varepsilon = 0 \quad \text{on } (0, T) \times \Gamma_\varepsilon, \quad (24)$$

$$\varepsilon^2 \nabla \tilde{\Phi}_\varepsilon \cdot \nu = 0 \quad \text{on } (0, T) \times \partial\Omega. \quad (25)$$

Theorem 4.11. *Let the a priori estimates of Theorem 3.6 be valid. Then the following two-scale limits can be identified for the electrostatic potential $\tilde{\Phi}_\varepsilon$ and the gradient $\varepsilon \nabla \tilde{\Phi}_\varepsilon$: There exists $\tilde{\Phi}_0 \in L^2((0, T) \times \Omega; H_{\text{per}}^1(Y))$ such that, up to a subsequence,*

$$\begin{aligned} \tilde{\Phi}_\varepsilon(t, x) &\xrightarrow{2} \tilde{\Phi}_0(t, x, y), \\ \varepsilon \nabla \tilde{\Phi}_\varepsilon(t, x) &\xrightarrow{2} \nabla_y \tilde{\Phi}_0(t, x, y). \end{aligned}$$

PROOF. We consider the estimate (7) in Theorem 3.5 which implies

$$\|\tilde{\Phi}_\varepsilon\|_{L^2(\Omega)} + \varepsilon\|\nabla\tilde{\Phi}_\varepsilon\|_{L^2(\Omega)} \leq C.$$

Theorem 4.2 then ensures the existence of the two-scale limit functions.

Theorem 4.12. *Let $(v_\varepsilon, p_\varepsilon, \Phi_\varepsilon, c_\varepsilon^+, c_\varepsilon^-)$ be a weak solution of Problem P_ε in the sense of Definition 3.1. Assume that c_ε^\pm converge strongly to c_0^\pm in $L^2((0, T) \times \Omega)$. Then the two-scale limit of $\tilde{\Phi}_\varepsilon$ due to Theorem 4.11 satisfies the following equations:*

$$\bar{\Phi}_0(t, x) = \left(\int_{Y_l} \varphi_j(y) dy \right) (c_0^+(t, x) - c_0^-(t, x)).$$

PROOF. To prove Theorem 4.12 we choose $\psi_0(t, x, \frac{x}{\varepsilon})$ as test function in (23) which leads to

$$\int_0^T \int_\Omega \varepsilon \nabla \tilde{\Phi}_\varepsilon(t, x) \cdot \nabla \varepsilon \psi \left(t, x, \frac{x}{\varepsilon} \right) dx dt = \int_0^T \int_\Omega (c_\varepsilon^+(t, x) - c_\varepsilon^-(t, x)) \psi \left(t, x, \frac{x}{\varepsilon} \right) dx dt.$$

We then pass to the two-scale limit $\varepsilon \rightarrow 0$ using the properties we have stated in Theorem 4.11:

$$\int_0^T \int_{\Omega \times Y_l} \left(\nabla_y \tilde{\Phi}_0(t, x, y) \cdot \nabla_y \psi(t, x, y) \right) dy dx dt = \int_0^T \int_{\Omega \times Y_l} (c_0^+(t, x) - c_0^-(t, x)) \psi(t, x) dy dx dt$$

After integration by parts with respect to y , the strong formulation for $\tilde{\Phi}_0$ may be read off:

$$\begin{aligned} -\Delta_y \tilde{\Phi}_0(t, x, y) &= c_0^+(t, x) - c_0^-(t, x) && \text{in } (0, T) \times \Omega \times Y_l, \\ \tilde{\Phi}_0 &= 0 && \text{in } (0, T) \times \Omega \times \Gamma, \\ \tilde{\Phi}_0 &&& \text{periodic in } y. \end{aligned}$$

Inserting the cell problem (18), we get

$$\bar{\Phi}_0 = \int_{Y_l} \tilde{\Phi}_0 dy = \left(\int_{Y_l} \varphi dy \right) (c_0^+ - c_0^-).$$

Remark 8 (Modeling of Φ_0). In the case $\alpha = 2$, it follows $\tilde{\Phi}_\varepsilon = \Phi_0^{\text{hom}} = \Phi_\varepsilon - \Phi_D$ and therefore

$$\bar{\Phi}_0 = \overline{\Phi_0^{\text{hom}} + \Phi_D} = \int_{Y_l} \Phi_0^{\text{hom}} + \Phi_D dy = \left(\int_{Y_l} \varphi dy \right) (c_0^+ - c_0^-) + |Y_l| \Phi_D.$$

The macroscopic representation is directly coupled to the macroscopic concentrations c_0^\pm . The case $\alpha < 1$ implies that Φ_ε and $\nabla \Phi_\varepsilon$ converge to Φ_D and zero, respectively. However, for any α an effective equation can be derived for the limit $\tilde{\Phi}_0$ of $\tilde{\Phi}_\varepsilon$.

4.2.2. Homogenized Limit Problems for Stokes' Equation

Theorem 4.13. *Let the a priori estimates of Theorem 3.6 be valid, i.e. especially $\beta \geq \alpha - 1$.*

Then the following two-scale limits can be identified for the velocity field \tilde{v}_ε and the gradient $\varepsilon \nabla \tilde{v}_\varepsilon$:

There exists $\tilde{v}_0 \in L^2((0, T) \times \Omega; H_{\text{per}}^1(Y))$ such that, up to a subsequence,

$$\begin{aligned} v_\varepsilon(t, x) &\xrightarrow{2} v_0(t, x, y), \\ \varepsilon \nabla v_\varepsilon(t, x) &\xrightarrow{2} \nabla_y v_0(t, x, y). \end{aligned}$$

The convergence for p_ε is standard, see [12] and we follow directly the procedure there including the right hand side which is due to the electrostatic interaction.

Theorem 4.14. *Let $(v_\varepsilon, p_\varepsilon, \Phi_\varepsilon, c_\varepsilon^+, c_\varepsilon^-)$ be a weak solution of Problem P_ε in the sense of Definition 3.1. Assume that c_ε^\pm converge strongly to c_0^\pm in $L^2((0, T) \times \Omega)$.*

For $\beta \geq \alpha - 1$ the two-scale limit of v_ε due to Theorem 4.13 satisfies the following equations:

$$\begin{aligned} \bar{v}_0(t, x) &= \int_{Y_l} v_0(t, x, y) dy = -K \nabla_x p_0(t, x) && \text{in } (0, T) \times \Omega, \\ \nabla_x \cdot \bar{v}_0(t, x) &= 0 && \text{in } (0, T) \times \Omega. \end{aligned}$$

PROOF. Choosing $\varepsilon \psi(x, \frac{x}{\varepsilon})$ as test function, it follows analogously to the proof of Theorem 4.8 that $p_0 = p_0(x)$ holds.

Defining the space $V_\psi = \{\nabla_y \cdot \psi = 0, \nabla_x \cdot \int \psi dy = 0, \psi = 0 \text{ on } (0, T) \times \Omega \times Y_s\}$ and choosing $\psi(x, \frac{x}{\varepsilon}) \in V_\psi$ as test function, leads in the limit $\varepsilon \rightarrow 0$ to

$$\int_0^T \int_{\Omega \times Y_l} \nabla_y v_0 \cdot \nabla_y \psi - p_0 \nabla_x \cdot \psi dy dx dt = \begin{cases} \int_0^T \int_{\Omega \times Y_l} -(c_0^+ - c_0^-) \nabla_y \Phi_0 \psi dy dx dt, & \beta = \alpha - 1 \\ 0, & \beta > \alpha - 1 \end{cases}$$

We now follow the proof of Theorem 4.8. Finally, integration by parts results in

$$-\Delta_y v_0(t, x, y) + \nabla_x p_0(t, x) + \nabla_y p_1(t, x, y) = \begin{cases} -(c_0^+(t, x) - c_0^-(t, x)) \nabla_y \tilde{\Phi}_0(t, x, y), & \beta = \alpha - 1 \\ 0, & \beta > \alpha - 1 \end{cases}$$

In the case $\beta = \alpha - 1$, we define the modified pressure $\tilde{p}_1 = p_1 + (c_0^+ - c_0^-) \tilde{\Phi}_0$. This allows to determine a standard incompressible Darcy's Law and finishes the proof of Theorem 4.14.

Remark 9 (Modeling of \bar{v}_0). The fluid flow is determined by a standard Darcy's law. The is no direct coupling to the electrostatic potential, since it is only present in the modified pressure term \tilde{p}_1 .

4.2.3. Homogenized Limit Problems for the Nernst-Planck Equations

Theorem 4.15. *Let the estimates of Theorem 3.6 be valid. Then the following two-scale limits can be identified for the concentration fields c_ε^\pm and their gradients ∇c_ε^\pm : There exist functions $c_0(t, x) \in L^2((0, T); H^1(\Omega))$ and $c_1(t, x, y) \in L^2((0, T) \times \Omega; H_{per}^1(Y))$ such that (up to a subsequence)*

$$\begin{aligned} c_\varepsilon^\pm(t, x) &\rightarrow c_0(t, x), \\ \nabla c_\varepsilon^\pm(t, x) &\xrightarrow{2} \nabla_x c_0(t, x) + \nabla_y c_1^\pm(t, x, y). \end{aligned}$$

PROOF. The statement of strong convergence holds true due to the extension of the concentration fields c_ε^\pm with the properties defined in Theorem 4.3 and Aubin-Lions compact embedding lemma.

Remark 10. The strong convergence of the concentrations c_ε^\pm in $L^2(0, T; L^2(\Omega))$ enables us to pass to the limit $\varepsilon \rightarrow 0$ also in the convective and drift term of the Nernst-Planck equations (5d).

Theorem 4.16. *Let $(v_\varepsilon, p_\varepsilon, \Phi_\varepsilon, c_\varepsilon^+, c_\varepsilon^-)$ be a weak solution of Problem P_ε in the sense of Definition 3.1. Assume that $\nabla \Phi_\varepsilon$ and v_ε two-scale converges as stated in Theorem 4.11 and Theorem 4.13. Then the two-scale limits of the concentrations as stated in Theorem 4.15 satisfy the following macroscopic limit equations:*

$$\begin{aligned} |Y_l| \partial_t c_0^\pm(t, x) + \nabla_x \cdot (\bar{v}_0(t, x) c_0^\pm(t, x) - D \nabla_x c_0^\pm(t, x)) &= |Y_l| R_0^\pm(c_0^+(t, x), c_0^-(t, x)) \quad \text{in } (0, T) \times \Omega, \\ (\bar{v}_0(t, x) c_0^\pm(t, x) - D \nabla_x c_0^\pm(t, x)) \cdot \nu &= 0 \quad \text{on } (0, T) \times \partial\Omega. \end{aligned}$$

PROOF. We choose $\varphi_3 = \psi_0(t, x) + \varepsilon \psi_1\left(t, x, \frac{x}{\varepsilon}\right)$ as test functions in the Nernst-Planck equations (5d).

$$\begin{aligned} \int_0^T \int_\Omega c_\varepsilon^\pm(t, x) \partial_t \left(\psi_0(t, x) + \varepsilon \psi_1\left(t, x, \frac{x}{\varepsilon}\right) \right) &+ (v_\varepsilon(t, x) c_\varepsilon^\pm(t, x) + \nabla c_\varepsilon^\pm(t, x) \pm \varepsilon^\gamma c_\varepsilon^\pm \nabla \Phi_\varepsilon(t, x)) \\ &\cdot \nabla \left(\psi_0(t, x) + \varepsilon \psi_1\left(t, x, \frac{x}{\varepsilon}\right) \right) dx dt \\ &= \int_0^T \int_\Omega R_\varepsilon^\pm(c_\varepsilon^+(t, x), c_\varepsilon^-(t, x)) \left(\psi_0(t, x) + \varepsilon \psi_1\left(t, x, \frac{x}{\varepsilon}\right) \right) dx dt. \end{aligned}$$

Passage to the limit $\varepsilon \rightarrow 0$ yields

$$\begin{aligned} \int_0^T \int_{\Omega \times Y} -c_0^\pm(t, x) \partial_t \psi_0(t, x) &+ (-v_0(t, x, y) c_0^\pm(t, x) + (\nabla c_0^\pm(t, x) + \nabla_y c_1^\pm(t, x, y)) \\ &\pm \left\{ \begin{array}{ll} c_0^\pm \nabla_y \Phi_0(t, x, y)) \cdot (\nabla_x \psi_0(t, x) + \nabla_y \psi_1(t, x, y)) dy dx dt, & \gamma = \alpha - 1 \\ 0, & \gamma > \alpha - 1 \end{array} \right\} \\ &= \int_0^T \int_{\Omega \times Y} R_0^\pm(c_0^+(t, x), c_0^-(t, x)) \psi_0(t, x) dy dx dt. \end{aligned}$$

We define

$$\tilde{c}_1^\pm = c_1^\pm \pm \left\{ \begin{array}{ll} c_0^\pm \nabla_y \Phi_0, & \gamma = \alpha - 1 \\ 0, & \gamma > \alpha - 1 \end{array} \right\}$$

and choose $\psi_0 \equiv 0$, which leads, after integration by parts with respect to y to:

$$\begin{aligned} -\Delta_y \tilde{c}_1^\pm(t, x, y) &= 0 & \text{in } (0, T) \times \Omega \times Y_l, \\ \nabla_y \tilde{c}_1^\pm(t, x, y) \cdot \nu &= -\nabla_x c_0^\pm(t, x) \cdot \nu & \text{on } (0, T) \times \Omega \times \Gamma, \\ \tilde{c}_1^\pm(t, x, y) & & \text{periodic in } y. \end{aligned}$$

The linearity of the equation yields (22) as representations for \tilde{c}_1^\pm supplemented by the family of cell problems (15).

On the other hand, if we choose $\psi_1(t, x, y) = 0$, we read off the strong formulation for c_0^\pm after integration by parts with respect to x and after inserting the representation (22) of \tilde{c}_1^\pm :

$$\begin{aligned} |Y_l| \partial_t c_0^\pm(t, x) + \nabla_x \cdot (\bar{v}_0(t, x) c_0^\pm(t, x) - D \nabla_x c_0^\pm(t, x)) &= |Y_l| R_0^\pm(c_0^+(t, x), c_0^-(t, x)) \quad \text{in } (0, T) \times \Omega, \\ (-\bar{v}_0(t, x) c_0^\pm(t, x) + D \nabla_x c_0^\pm(t, x)) \cdot \nu &= 0 \quad \text{on } (0, T) \times \partial\Omega, \end{aligned}$$

with \bar{v}_0, D being defined in (14) and (21), respectively.

Remark 11 (Modeling of c_0^\pm). The transport of the concentrations is determined by a convection-diffusion-reaction equation. There is no direct coupling to the electrostatic potential, since it is only present in the modified higher order concentration term \tilde{c}_1 . Depending on the choice of β , the effective equations might be coupled only in one direction.

5. Discussion

We wish to point out the following aspects:

In Section 4, we considered the rigorous passage to the two-scale limit $\varepsilon \rightarrow 0$ for different boundary conditions of the electrostatic potential and different ranges of the scale parameter (α, β, γ) and have derived the corresponding two-scale limits of Problem P_ε . We classified *conceptually different types of limit systems*. In all cases, auxiliary cell problems need to be solved to be able to provide closed-form expressions for the effective macroscopic coefficients. Depending on chosen model, the macroscopic problem is coupled only in one direction or fully coupled. Solving these problems numerically is computationally challenging due to the mass balances that have to be fulfilled and the diverse boundary conditions, especially periodic ones. The most crucial point is that an appropriate fixed point iteration has to be constructed depending on the nature of the nonlinear couplings. Moreover, corrector estimates will be needed in order to make it possible to compare the effective solutions/problem descriptions with the oscillatory solution/microscopic model. The different structures of the resulting effective equations of the homogenization process are underlined in Remark 4, Remark 5, Remark 7 for Neumann boundary conditions for the electrostatic potential (i. e. given surface charge) and in Remark 8, Remark 9, Remark 11 for Dirichlet boundary conditions for the electrostatic potential (i. e. given ζ potential). In the colloid literature, one can also find the so called perfect sink boundary condition for the concentration fields instead of the no-penetration boundary condition, i.e. $c_\varepsilon^\pm = 0$ on $(0, T) \times \Gamma_\varepsilon$. In the framework of homogenization this would lead together with the strong convergence of the concentration fields to $c_0^\pm \equiv 0$ as limit. Obviously, this does not provide a suitable model for colloidal transport phenomena.

The following question arises naturally: *Given a particular scenario of colloidal transport in the soil, which is the best/most reasonable mathematical (limit) model that should be considered?* Answering this question is not limited to choosing the precise values for the choice of the appropriate boundary conditions and the scale range (α, β, γ) . It also requires a careful calibration of the model by an intensive numerical testing of the chosen set of limit equations. Further adjustment by experimental measurements and parameter identification procedure may need to be done to make the model quantitatively.

It is worth noting that, using two-scale convergence, we could not pass to the limit $\varepsilon \rightarrow 0$ for all choices of the parameter ranges. However, in these cases formal two-scale asymptotic expansions can be applied in order to pass formally to the limit $\varepsilon \rightarrow 0$ using the transformation $u^\pm := \exp(\mp\Phi) c^\pm$ which arises especially when treating drift diffusion problems (compare, e.g. [26, 19]).

An alternative is to treat a linearized system as has been considered via rigorous homogenization in the stationary case in [2].

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